Effect of nitrate nitrogen content on properties of modified single-base propellant

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Abstract—In order to investigate the effect of nitrocellulose (NC) nitrogen on the performance of modified single-base propellants, modified single base propellants with different nitrogen content (12.8%, 12.7%, 12.6%, 12.4%) were prepared by solvent extrusion. The mechanical properties of the modified single-base propellant were tested using a universal material testing machine and a simply supported beam impact tester; the impact section was observed by a scanning electron microscope; and the combustion performance of the modified single-base propellant was tested by a closed explosive device test. The results showed that the higher the nitrogen content of nitrocellulose, the worse the swelling effect, the worse the cotton's dissolving ability, and the worse the mechanical properties of modified single-base propellant; while the nitrogen content increases, the burning rate and force capacity of the propellant gradually increase.

1. INTRODUCTION

Traditional single-base propellants have been unable to meet the energy requirements of some advanced weapons due to their low energy \cite{1}. Adding hexogen (RDX) on the basis of single-base propellant can increase energy, but the mechanical properties of modified single-base propellant will be affected with the increase of RDX content. The cotton blending method can improve the mechanical properties of the modified single base medicine containing RDX\cite{2,3}. Therefore, the nitrogen content of nitrocellulose is an important research direction to improve the mechanical properties of the modified single base medicine and maintain its excellent combustion stability.

Zheng Lin, etc. \cite{4} used the existing mechanical property testing methods of China to test the low-temperature mechanical properties of the diazidonitrazapentane propellant, and found that the propellant made from nitrocellulose with a nitrogen content of 12.6% at \(-40^\circ C\) has better mechanical properties than Nitrocellulose has a propellant with a nitrogen content of 13.0%. Chai Hua, etc. \cite{5} analyzed the macro and micro structures of NC samples with different nitrogen contents. It was found that in the main stage of pyrolysis, NC with higher nitrogen content will produce more kinds of gas, and more cyclization and recombination forms will occur in the post-reaction stage of pyrolysis.
In this study, modified single-base propellants with different nitrogen contents (12.8%, 12.7%, 12.6%, 12.4%) were prepared. The effects of nitrogen content of different nitrocellulose on the mechanical properties and combustion properties of modified single-base propellant were studied, in order to provide reference for the research and application of modified single-base propellant.

2. EXPERIMENTAL

2.1. Materials
NC (nitrogen content is 13.15% and 11.85%) was provided by Luzhou North Chemical Industry Company in China. RDX provided by Gansu Yinguang Chemical Industry Group Corporation. Analytical pure specifications of 2, 4-dinitrotoluene (DNT) and diphenylamine (DPA) provided by Sinopharm Chemical Reagent Company in China. Analytical grade acetone and absolute ethanol provided by Nanjing Chemical Reagent Company in China.

2.2. Measuring apparatus
JH-500 kneading machine, ZJB-30 hydraulic press, Tianjin Second Forging Press Machine Factory; Instron 3367 universal material testing machine, American Instron Corporation; JJ-20 pendulum impact testing machine, Changchun Intelligent Instrumentation Equipment Co., Ltd Company; Quanta250 SEM, American FEI Company.

2.3. Sample preparation
The modified single-base propellant formulation used in this experiment is shown in Tab. 1.

| Sample | ω (%) | f (kJ·kg⁻¹) | α (cm³·g⁻¹) |
|--------|-------|-------------|-------------|
| 1      | 12.8% | 947.24      | 0.93        |
| 2      | 12.7% | 940.59      | 0.93        |
| 3      | 12.6% | 934.85      | 0.91        |
| 4      | 12.4% | 910.14      | 0.90        |

The solvent method extrusion molding process was used to prepare 15/1 single-hole tubular pellets and dumbbell-shaped tablets with a length of 40.0mm, 60.0mm and an aspect ratio of 1: 1. Drugs of different specifications are first dissolved by wet baking, and then the remaining moisture is removed by dry baking, and the moisture requirement is less than 0.5%.

2.4. Mechanical properties
In this paper, according to the GJB770B-2005 standard, the impact test sample is a tubular drug with a length of 60.0mm, the tensile test sample is a dumbbell-shaped sheet with a thickness of 1.0mm, and the compression test sample is a tubular drug with an aspect ratio of 1: 1. During the test, control the tensile and compression speed to 10mm·min⁻¹. Before the test, the sample should be kept at least 4 hours under the conditions of high temperature (50℃), normal temperature (20℃) and low temperature (-40℃). At least 5 valid results were obtained for each sample, and the results of the experiment were averaged.
2.5. Sample preparation

A closed explosive device with a volume of 104.17 cm$^3$ was used to test the static combustion performance of a 15/1 modified single base propellant with a length of 40.0 mm. The test conditions were a packing density of 0.2 g cm$^{-3}$, a test temperature of -40°C, 20°C, and 50°C, and an ignition pressure of 10.98 MPa. The p-t curve measured by the closed explosive test is processed to obtain the u-p curve.

3. Results and discussion

3.1. Mechanical properties of modified single-base propellants

The tensile, compressive, and impact strength of the modified single-base propellant was tested at different temperatures. The test results are shown in Tab. 2, Tab. 3 and Tab. 4.

| TABLE 2. TENSILE STRENGTH OF MODIFIED SINGLE-BASE PROPELLANTS |
|---------------------------------------------------------------|
| Sample | $\sigma_c$ (MPa) |
| -40°C | 20°C | 50°C |
| 1 | 106.33 | 106.05 | 91.16 |
| 2 | 125.57 | 106.72 | 105.60 |
| 3 | 126.51 | 117.66 | 110.60 |
| 4 | 136.09 | 130.48 | 122.34 |

| TABLE 3. COMPRESSIVE STRENGTH OF MODIFIED SINGLE-BASE PROPELLANTS |
|------------------------------------------------------------------|
| Sample | $\sigma_b$ (MPa) |
| -40°C | 20°C | 50°C |
| 1 | 69.73 | 58.61 | 50.89 |
| 2 | 75.29 | 63.46 | 51.87 |
| 3 | 76.05 | 65.01 | 52.50 |
| 4 | 78.28 | 67.20 | 53.31 |

| TABLE 4. IMPACT STRENGTH OF MODIFIED SINGLE-BASE PROPELLANTS |
|---------------------------------------------------------------|
| Sample | $\sigma_k$ (kJ m$^{-2}$) |
| -40°C | 20°C | 50°C |
| 1 | 8.54 | 12.68 | 13.71 |
| 2 | 12.59 | 16.98 | 19.17 |
| 3 | 13.94 | 17.54 | 20.36 |
| 4 | 14.73 | 20.17 | 22.89 |

As can be seen from Tab. 2, Tab. 3 and Tab. 4 under different temperature conditions, as the nitrogen content of nitrocellulose decreases, the tensile, compressive and impact strengths of the modified single-base propellant become higher and higher.

The mechanical properties of the propellant are related to the solubility of the nitrocellulose. As the content of D cotton soluble in the alcohol and ketone solvent increases in the mixed nitrocellulose, the dissolved part of the D cotton is coated and penetrates into the expansion body of the B cotton, which
enhances Mechanical properties of modified single base propellants. Figure 1 are SEM images of the low-temperature impact section of different modified single-base propellants at 2000 times.

a) SEM image of sample 1

b) SEM image of sample 2

c) SEM image of sample 3
From Fig. 1, it can be seen that as the nitrogen content of NC in the modified single-base propellant increases, the more uniform the component distribution in the modified single-base propellant, the better the impact strength of the modified single-base propellants. Based on the test results, the reasons why the nitrogen content of NC affects the mechanical properties of modified single-base propellant may be: The NC macromolecule is a polymer system. Because the nitrocellulose in the mixed nitrocellulose has a nitrogen content of 13.15%, the nitrocellulose has a large binding energy and can only be in a swelling state. In the mixed solvent, as the nitrogen content of the modified single-base propellant increases, the amount of NC (13.15%) used also increases, and the plasticized quality of the mixed nitrocellulose swelling cannot be guaranteed. As the nitrogen content increases, the number of nitro-substituted hydroxyl groups increases, and the hydroxyl groups are gradually esterified. The number of hydrogen bonds formed directly with polar oxygen atoms in solid fillers such as RDX in the formula decreases, and the force between hydrogen bonds decreases. The interaction between molecular chains is reduced, which reduces its ability to bind to solid fillers, resulting in poor mechanical properties of modified single-base propellants. The lower the nitrogen content of the mixed nitrocellulose, the more NC (11.85%) components in the mixed cotton, the more NC is dissolved in the alcohol and ketone solvent, and the more difficult to dissolve other fillers are more evenly distributed on the single base. In the drug matrix, the degree of polymerization is large, the plasticizing performance is better, the toughness of the modified single-base propellant is improved, and the mechanical properties of the propellant are improved.

3.2. Combustion performance of modified single-base propellants
In order to study the effect of nitrocellulose nitrogen content on the combustion performance of modified single-base propellant, a closed explosive test was performed on the modified single-base propellant sample. The test results are shown in Fig. 2.
It can be seen from Fig. 2 that the time for each sample to reach the same pressure in the pressure range of 11MPa to 210MPa is sample 1, sample 2, sample 3, and sample 4, that is, as the nitrogen content of the nitrocellulose increases, the end time of combustion decreases. The slope of the burning rate and burning rate pressure curve of the sample decreased with the decrease of the nitrogen content of the nitrocellulose. Compared with the other three samples, the burning rate of the modified single-base propellant with a nitrogen content of 12.4% significantly increased the burning time, the pressure curve changed slowly during the initial combustion stage, and the pressure rising rate, burning rate and burning rate rising rate were low.

Tab. 5 shows the performance parameters such as the burning rate coefficient and burning rate pressure index of modified single-base propellants with different NC nitrogen content. Among them, $p_m$ is the maximum pressure of combustion, $t_m$ is the end time of combustion, $n$ is the burning rate pressure index, $u_1$ is the burning rate coefficient, and $p_{dpm}$ is the pressure value when the maximum pressure is steep. All samples have a burning rate pressure index of less than 1 in the low pressure range (50 to 100MPa); all samples have a burning rate pressure index greater than 1 in the medium pressure range (100 to 150MPa); only sample 3 have pressure in the high pressure range (150MPa to $p_{dpm}$). The index is greater than sample 1. From the entire pressure range (50MPa to $p_{dpm}$), the sample burning rate pressure index is less than 1. The burning rate pressure index of the sample did not change significantly with the increase of nitrogen content of NC, and was less affected by the nitrogen content of NC.
TABLE 5. THE BURNING RATE COEFFICIENT AND PRESSURE INDEX OF MODIFIED SINGLE-BASE PROPELLANT WITH DIFFERENT NITROGEN CONTENT

| Sample | $p_m$ (MPa) | $t_m$ (s) | $u_l$ | $n$ | $p_{50-100}$ (MPa) | $p_{100-150}$ (MPa) | $p_{150-\rho_{qpm}}$ (MPa) | $p_{50- \rho_{qpm}}$ (MPa) | $\rho_{qpm}$ |
|--------|-------------|-----------|-------|-----|-------------------|-------------------|-------------------------|-------------------------|-----------|
| 1      | 233.10      | 18.77     | 0.0853| 0.9410| 0.0612           | 1.0108            | 0.0927                  | 0.0819                  | 200.15    |
| 2      | 231.17      | 19.67     | 0.0851| 0.9291| 0.0547           | 1.0239            | 0.0646                  | 0.0746                  | 203.49    |
| 3      | 231.03      | 20.61     | 0.0611| 0.9601| 0.0427           | 1.0368            | 0.0482                  | 0.0553                  | 201.12    |
| 4      | 224.27      | 24.17     | 0.0853| 0.9410| 0.0612           | 1.0108            | 0.0925                  | 0.0950                  | 200.23    |

4. CONCLUSIONS
The larger the nitrogen content of mixed nitrocellulose, the more NC (13.85%), the worse its swelling effect, the worse the cotton's dissolving ability, and the worse the mechanical properties of modified single-base propellant. Under the conditions of high temperature, normal temperature and low temperature, the tensile strength, compressive strength and impact strength all increase with the decrease of nitrogen content of nitrocellulose.

Under a certain pressure condition, the burning rate and the slope of the burning rate pressure curve of the modified single-base propellant decrease as the nitrogen content of the nitrocellulose decreases. The burning rate pressure index is less affected by the nitrogen content of nitrocellulose. As the nitrogen content of nitrocellulose decreases, the force capacity and covolume of the modified single-base propellant decrease.

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