

Thermal Analysis of a Certain Type of High Energy Propellant

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Abstract. In order to study the thermal decomposition characteristics of four component HTPB propellants, the thermo gravimetric analysis (TG) experiment was carried out. The TG curves of propellants at different temperatures, and the TG curves of different components of propellants at the same temperature were obtained, and the kinetic parameters at different heating rates were calculated. In general, the heat of the solid propellant was found. Decomposition is a continuous process with thermal stability and thermal safety.

1. Introduction

Composite solid propellant is a composite material with polymer matrix and solid particles as filler. It has strong nonlinear characteristics. During long-term storage, propellants are affected by external factors such as temperature and strain, and their microstructure will change, resulting in complex constitutive responses [1]. Propellants are mainly composed of oxidant, metal fuel (metal powder or non-metal powder, fiber), polymer binder prepolymer, curing agent and plasticizer. At present, the commonly used composite solid propellants are composed of hydroxyl terminated polybutadiene (HTPB), aluminum (AL) and ammonium perchlorate (AP) [2]. High energy propellant with RDX/Al/AP as the main energy component is widely used in long range rocket launchers and other rocket launcher ammunition engines.

In the long-term storage process, propellants will undergo slow thermal decomposition, which will cause unpredictable danger in storage and use. Therefore, it is of great significance to study the thermal decomposition properties of the solid propellant. The thermo gravimetric analysis (TG) is carried out to study the thermal decomposition and thermal safety of a certain type of double base propellant after aging. The parameters of the thermal decomposition reaction are calculated and the variation of thermal properties is found through calculation and test, which can provide basic support for the extension of the propellant.

2. Experiment

2.1. Sample size and composition

The main components of HTPB/RDX/Al/AP four component propellants are: hydroxyl terminated polybutadiene (HTPB) 7%, aluminum (AL) 14%, black cord gold (RDX) 9%, ammonium perchlorate 65%, and other components including isophorone diisocyanate (IPDI) and sebacic acid two simplistic (DOS). The sample mass is 2mg to 3mg.



2.2. Instrument and test conditions

TG test: the Pyris-1 type thermo gravimetric analyzer is used for the test; nitrogen (99.999%), the pressure is 0.3MPa, the dynamic atmosphere, the flow rate is $2.5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $15\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, from $100\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$.

3. Results Analysis

The TG thermal decomposition experiment of the propellant and its components at the same temperature is obtained by graph 1.

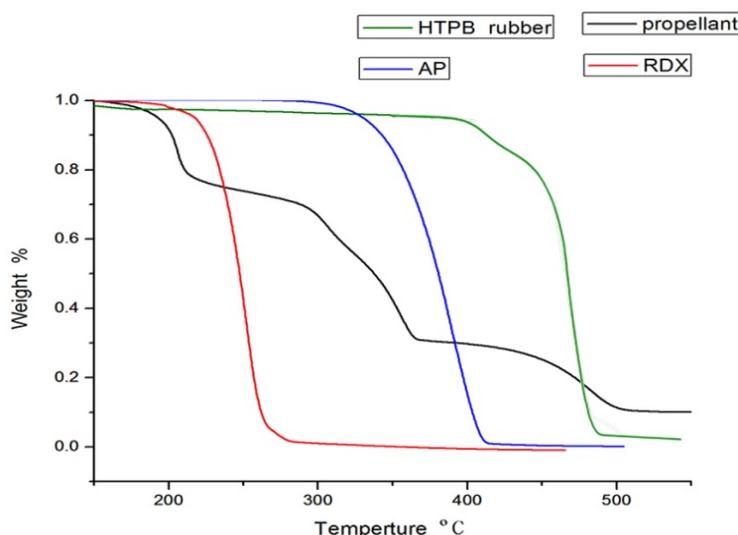


Figure 1. the TG curve of the composition of the propellant

It can be seen from Fig. 1 that there are three weightlessness steps in the TG curve of propellants. The first step generally occurs in the range of $150\sim 220\text{ }^{\circ}\text{C}$, and the weight loss of propellant reaches about 20% at about $20\text{ }^{\circ}\text{C}$. Second weightless steps are roughly in the range of $220\sim 360\text{ }^{\circ}\text{C}$, the weight loss reaches about 70% at about $370\text{ }^{\circ}\text{C}$. The third weightlessness steps appeared in the range of $360\text{ }^{\circ}\text{C}$ to $515\text{ }^{\circ}\text{C}$, and the weightlessness reached about 90% at $515\text{ }^{\circ}\text{C}$. The remaining residue is about 10%. The RDX was pyrolyzed between $165\sim 270\text{ }^{\circ}\text{C}$ and no residue; AP was decomposed with no residue between $265\sim 400\text{ }^{\circ}\text{C}$, and the rubber was decomposed between $450\sim 550\text{ }^{\circ}\text{C}$ and no residue. Analysis shows that the first weightlessness step of propellant is mainly divided into three parts. The thermal decomposition of RDX produces gas and occurs weightlessness. Isophorone diisocyanate (IPDI) and two octyl sebacate (DOS) are heated to decompose and lose weight, and isophorone diisocyanate (IPDI) can react with the oxidant, which will lead to the premature reaction of partial AP to produce gas and weightlessness. This stage accounts for about 20%; Second weightless steps are thermal decomposition of AP, and third weightless steps are low temperature decomposition and high temperature decomposition and thermal decomposition of rubber after the transformation of AP [3], and the remaining part of AL powder and reaction residue.

4. Calculation of kinetic parameters of thermal analysis

Under the conditions of heating rate of $2.5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and $15\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, the propellant samples were tested in the Pyris-1 thermo gravimetric analyzer, and the TG curves were obtained. Fig. 2 is a TG curve with heating rate of $2.5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and $15\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

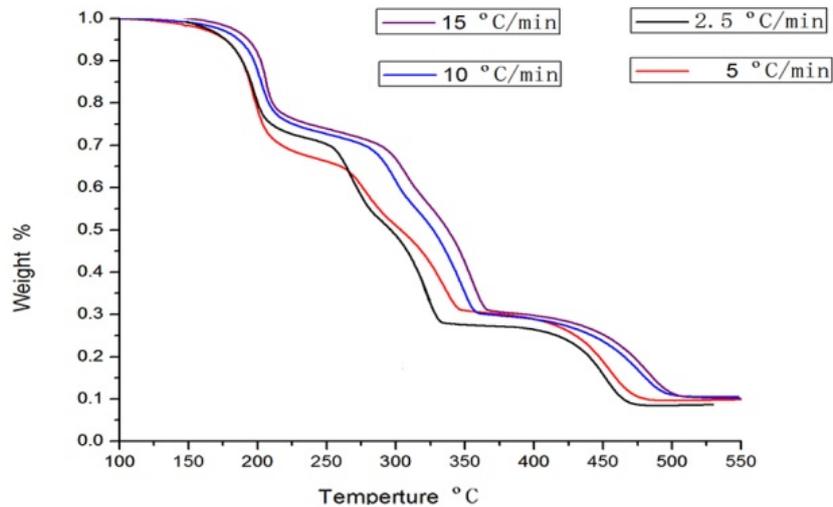


Figure 2. TG curve of propellant

(1) Integral method

In this paper, the Flynn-Wall-Ozawa [4] method is used to solve the problem, The Equation is as follows:

$$\lg(\beta) = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567 \frac{E}{RT} \quad (1)$$

By the linear relation of $\lg(\beta) - 1/T$, the E value of the slope is obtained by the slope.

In the formula, A is the mechanism function, α is the reaction depth; T is the reaction temperature (K); A is the pre index factor; $R=8.314\text{J}/(\text{mol} \cdot \text{K})$ is the molar gas constant; the beta is the heating rate ($^{\circ}\text{C}/\text{min}$); E is the reactive activation energy ($\text{KJ} \cdot \text{mol}^{-1}$).

(2) Differential method

In this paper, the Starink [4] method is used to solve the problem, The Equation is as follows:

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = C_s - 1.0037 \frac{E}{RT} \quad (2)$$

In the formula, C_s is constant, and the other parameters have the same meaning as (1).

The activation energies E of different reaction depths were calculated by the above two methods. The results are shown in Table 1.

Table 1. activation energy of different reaction depth of propellant (TG)

α	E /KJ·mol ⁻¹	
	integral method (Ozawa)	Differential method (Starink)
0.1	186.961	189.871
0.15	185.012	186.112
0.2	210.701	212.249
0.3	167.047	170.901
0.35	175.779	175.880
0.4	165.485	168.197
0.5	187.488	189.116
0.6	202.271	205.049
0.65	196.662	197.663

5. Conclusion

There are three weightlessness steps in the TG curve of propellants. The first step generally occurs in the range of 150 ~ 220 °C, Analysis shows that the first weightlessness step of propellant is mainly divided into three parts. The thermal decomposition of RDX produces gas and occurs weightlessness. Isophorone diisocyanate (IPDI) and two octyl sebacate (DOS) are heated to decompose and lose weight, and isophorone diisocyanate (IPDI) can react with the oxidant, which will lead to the premature reaction of partial AP to produce gas and weightlessness. This stage accounts for about 20%; Second weightless steps are roughly in the range of 220 ~ 360 °C, Analysis shows that Second weightless steps are thermal decomposition of AP. The third weightlessness steps appeared in the range of 360 to 515 °C, and the weightlessness reached about 90% at 515 °C. And third weightless steps are low temperature decomposition and high temperature decomposition and thermal decomposition of rubber after the transformation of AP. And the remaining part of AL powder and reaction residue. The activation energy of propellant is calculated to be between 166 and 212KJ mol⁻¹.

References

- [1] Dongmo Zhou, Xiangyang Liu, Qingyun Wang and so on. Constitutive damage characteristics of HTPB propellant under constant strain aging [J]. Propelling technology, 2017 38 (2): 442 - 448.
- [2] Wei Zhang, Paulownia, Xing Zhou and so on. Rocket propellant [M]. Beijing: National Defense Industry Press.
- [3] Gong Shan. Preparation of Carbon-Base Composite Particles and Their Catalytic Performances for Thermal Decomposition of Ammonium Perchlorate [D]. Harbin: Harbin Institute of Technology, 2015.
- [4] Wenru Ceng, Bin Yao, Ruo Wen Zong, et al. The relationship between the activation energy and conversion of polystyrene pyrolysis reaction [J]. polymer materials science and engineering, 2008, 24 (8): 129 - 130.