Effect of Antioxidant on Storage Performance and Life Prediction of HTPB Propellant

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Abstract. In order to study the aging property of HTPB propellant in storage and the effect of antioxidant on the storage life of propellant, accelerated aging tests were carried out for two types of propellant. A non-linear aging model was introduced into the classical Arrhenius equation, and the starting point of aging was modified. With the maximum elongation as the evaluation parameter, the storage life at 25°C is 9.6 years with the critical value is 20%, and the storage life is 17.5 years with the critical value is 15%. By controlling the content of antioxidant in propellant, the formula of type I propellant was modified, and the life of propellant after modification was predicted. The storage life is 12.4 years at 25°C with the critical value is 20%, and the storage life of propellant is 21.3 years when the critical value is 15%. It was proved that the storage life of propellant could be effectively improved by controlling the content of antioxidant.

1. Introduction

HTPB composite solid propellant is an energetic composite material based on polymer and filled with metal powder and oxidant. It is an important power source of rocket engine. Its performance will have a direct impact on the combat capability of rocket [1]. The physical and chemical properties of propellant will change under the load/environment spectrum during storage, which will lead to the deterioration of the mechanical properties of propellant and the bonding properties of various bonding interfaces of rocket motor grain with the increase of storage time. Especially when the propellant of rocket engine is integrally adherent casting, the charge cannot be replaced during service [2]. The main cause of propellant deterioration is the slow chemical changes during storage. At present, it is generally believed that the main reaction is the oxidation, branching and cracking of polymer under the action of oxidant and air (oxygen and water vapor). For HTPB propellants, the aging reaction caused by double bond oxidation is more important [3, 4]. In order to prolong the life of HTPB propellant, many scholars have studied the effect of antioxidant on the performance of HTPB propellant. In order to avoid the waste caused by early retirement and the harm caused by overdue service, it is necessary to accurately predict the storage life of solid propellant for rocket motor. To know exactly the storage life of a propellant, it is better to store propellant samples or propellant engines naturally. However, this method is not only expensive, but also time-consuming. In this paper, the change of mechanical properties of HTPB propellant under storage aging was studied by
accelerated aging. A non-linear aging model was introduced into Arrhenius formula to predict the storage life of HTPB propellant. The effect of antioxidant on storage performance and life of HTPB propellant was also studied. The content of antioxidant in the formula was revised, and the life of the revised formula was estimated.

2. Test section

2.1. Condition of Test
(1) Equipment: Type 402 and 802 thermal aging ovens with rotating speed of 12 min⁻¹ and natural convection of air.
(2) Samples: Cut into 10×25×100mm specimens and hang vertically in the aging oven. Dumbbell-shaped specimens were made before the test. The state of specimens was adjusted for 16-46 hours at room temperature, and then the performance was tested.
(3) Temperature control accuracy: ±2°C.

2.2. Test Results
Tensile strength (σₘ) and maximum elongation (εₘ) were measured for aged samples. The aging results of type I propellant with different content of antioxidant at 80°C are shown in Figure 1. The aging results of type I propellant with 0.1% content of antioxidant at 35°C, 50°C and 65°C are shown in Figure 2. For ease of comparison, the aging results of type II propellant at 80°C are listed in Figure 3. The first point is the starting point of accelerated aging. The time of this point is the correction time considering the effect of curing process on aging. The correction method is shown in Table 1.

![Figure 1](image1.png)

![Figure 2](image2.png)

**Table 1. Revised Aging Starting Point**

| Aging Temperature (K) | 298 | 308 | 323 | 338 | 343 | 353 |
|-----------------------|-----|-----|-----|-----|-----|-----|
| K(343)/K(T)           | 3.67| 2.58| 1.64| 1.12| 1   | 0.8 |
| Computation Time (d)  | 162 | 35.7| 9.7 | 4.7 | 4   | 3   |
| Approximate full time (d) | 162 | 36  | 10  | 5   | 4   | 3   |
Figure 2. The aging results of type I propellant with 0.1% content of antioxidant at 35°C, 50°C and 65°C

Figure 3. The aging results of type II propellant at 80°C

3. Selection of Aging Model
The basic teaching model of accelerated aging test is Arrhenius formula [6, 7]:

\[ K = A \exp \left( -\frac{E}{RT} \right) \]  \hspace{1cm} (1)

In formula: K is the rate constant of aging reaction at temperature T; A is the coefficient; E is the activation energy, J/mol; T is the absolute temperature, K; R is the general gas constant, 8.314 J/(mol·K).

According to the formula, the only effect of temperature is to increase the reaction rate, that is, K increases with the increase of temperature. Usually K is derived from the following formula [8]:

\[ P = K_1 t + a \]  \hspace{1cm} (2)

In the formula: K is a linear reaction rate constant; P is a physical property; a is a coefficient; t is time (d).

However, the test shows that the change of propellant performance cannot be described by formula (2) during the aging process of propellant. For example, by plotting time with the ε in Fig.1, it can be seen that the relationship between them is obviously not linear, that is, K is not a constant. However, if the logarithm of time is used to draw a graph, it is an ideal straight line, which can be expressed by the following formula:
In the formula, \( b \) is the coefficient and \( K_2 \) is the non-linear reaction rate constant.

By replacing \( K \) in formula (1) with \( K_2 \) and taking logarithm of formula (1), formula (4) is obtained:

\[
\lg K_2 = \lg A - \frac{E}{RT\ln 10}
\]

(4)

The storage time at room temperature can be extrapolated by substituting the previous test results into the formulas (3) and (4).

4. Data Processing

4.1. Selection of Evaluation Parameters and Determination of Critical Value

In the aging process of propellant, all kinds of parameters are changing, so it is necessary to select a suitable parameter as the evaluation parameter. From the point of view of use, the important index to ensure the integrity of rocket engine is \( \varepsilon_m \), so \( \varepsilon_m \) is taken as the evaluation parameter [9]. For different propellants and different engines, the critical value of marking the end point of aging should be different because of the different stress conditions. When the calculated value of polysulfide propellant charge is greater than 15% in an engine bonded with a certain shell, it is required that the \( \varepsilon_m \) be greater than 20%. In this paper, the \( \varepsilon_m=20\% \) and 15% are selected for comparison.

4.2. Revision of Aging Starting Time

In the curing process, aging reaction is also taking place, so the curing end point is not the starting point of aging. The solidification time of propellant at 70°C for 3 days can be calculated in 4 days, and the corresponding time at other temperatures can be modified by the following Arrhenius derivation [10]:

\[
\ln \frac{K(T+\Delta T)}{K(T)} = \frac{E}{RT\Delta T}
\]

(5)

By substituting the activation energy 21.338 kJ/mol into formula (5), the ratio of \( K \) value at different temperatures to \( K \) value at 70°C can be obtained. Assuming that \( (P-b) \) in formula (3) after curing is a certain value, it can be derived:

\[
\frac{K(343)}{K(T)} = \frac{\lg (t)}{\lg 4}
\]

(6)

It can be obtained that the curing time at 70°C for 4 days is equivalent to the aging time at different temperatures. The corrected results are shown in Table 1.

4.3. Result Calculation

Using the results of Figure 1 and 2, the regression equations corresponding to formula (3) at different temperatures containing 0.1% antioxidant are calculated as follows:

| Temperature (°C) | Regression Equation | Correlation Coefficient (r) |
|-----------------|---------------------|-----------------------------|
| 35°C            | \( \varepsilon_m = 81.91 - 23.391 \lg t \) | 0.989                       |
| 50°C            | \( \varepsilon_m = 80.66 - 33.341 \lg t \) | 0.973                       |
| 65°C            | \( \varepsilon_m = 79.81 - 46.284 \lg t \) | 0.988                       |
| 80°C            | \( \varepsilon_m = 69.34 - 53.934 \lg t \) | 0.987                       |

According to the \( K_2 \) value of the above regression equation, the regression equation corresponding to (4) is obtained as follows:
\[ \lg K_2 = 4.293 - 896.7 \frac{1}{T} \quad r = 0.992 \]  \tag{7}

\( K_2 = 19.21, E = 17.17 \text{ kJ/mol}, b = 88.14 \text{ at } 25^\circ C, \) and \( \varepsilon_m \) is 45.7\% at the beginning of aging, that is to say, the aging formula is as follows:

\[ \varepsilon_m = 88.14 - 19.21 \lg t \]  \tag{8}

By substituting the above formula, the storage life at 25\(^\circ\)C is 3524 days, that is, 9.6 years when the critical value \( \varepsilon_m \) is 20\%, and the storage life is 6417 days, that is, 17.5 years when the critical value \( \varepsilon_m \) is 15\%.

4.4. **Comparison with Type II Propellant and Revision of Formula**

In the absence of actual storage results, it is very useful to compare with the accelerated aging results of similar products. According to the results in Figure 3, the regression equation of 80\(^\circ\)C aging of type II propellant can be obtained as follows:

\[ \varepsilon_m = 56.36 - 37.33 \lg t \quad r = 0.970 \]  \tag{9}

The critical aging time (\( \varepsilon_m = 20\% \)) at 80\(^\circ\)C is 9.4 days, while the type I propellant containing 0.1\% antioxidant is only 8.2 days. This shows that its aging performance is not as good as that of type II propellant. Therefore, the content of antioxidant was increased to 0.17\% in the formulation. The aging regression equation of type I propellant containing 0.2\% antioxidant at 80\(^\circ\)C can be obtained by using the data in Figure 1 as follows:

\[ \varepsilon_m = 85.11 - 66.44 \lg t \quad r = 0.999 \]  \tag{10}

By interpolating it with the regression equation containing 0.1\% antioxidant, the aging equation with 0.17\% antioxidant can be obtained as follows:

\[ \varepsilon_m = 80.38 - 62.69 \lg t \]  \tag{11}

According to this equation, the critical aging time at 80\(^\circ\)C is 9.2 days, which is equivalent to the aging performance of type II propellant.

4.5. **Storage Life Prediction of Modified Formula**

Accelerated aging test was not carried out after formula modification. However, as can be seen from Figure 2, the influence of antioxidants on properties is regular, and there will not be much error in the calculation by interpolation method. Assuming that the activation energy of the projection remains unchanged, the Arrhenius formula of 0.17\% antioxidant formulation can be obtained as follows:

\[ \lg K_2 = 4.337 - 896.7 \frac{1}{T} \]  \tag{12}

The initial \( \varepsilon_m \) calculated by interpolation method is 50.0\%, and then the aging equation at 25\% can be obtained as follows:

\[ \varepsilon_m = 97.82 - 21.28 \lg t \]  \tag{13}

According to the critical value of 20\%, the storage life at 25\(^\circ\)C is 4539 days, that is 12.4 years. According to the critical value of 15\%, the storage life is 7796 days, that is 21.3 years.

5. **Conclusions**

In this paper, a non-linear aging model was introduced into the classical Arrhenius equation, and the storage life of HTPB propellant was predicted by the accelerated aging equation. The storage life of
type I propellant is 3524 days, that is, 9.6 years when the critical value is 20%, and the storage life is 6417 days, that is, 17.5 years when the critical value is 15%.

By controlling the content of antioxidant in propellant, the formula of type I propellant was modified, and the life of propellant after modification was predicted. When the critical value is 20%, the storage life is 12.4 years at 25℃. The storage life of propellant was 21.3 years when the critical value was 15%. It was proved that the storage life of propellant could be effectively improved by controlling the content of antioxidant.

From the regression equation, the correlation coefficients are all above 0.97, which shows that the mathematical model is in agreement with the experimental results, so the results are regrettable. However, there must be some differences between the hypothesis and the reality when establishing the digital model. In addition, interpolation and extrapolation will inevitably bring some errors. Its reliability needs to be further verified by actual storage.

References

[1] HOU Lin-fa. Composite solid propellant[M]. Beijing: China Aerospace Publishing House, 1994.
[2] PANG Ai-min. Theory and engineering of solid rocket propellant [M]. Beijing: China Aerospace Publishing House, 2014.
[3] ZHANG Xing-gao. Study on the aging properties and storage life prediction of HTPB propellant[D]. Changsha: National University of Defense Technology, 2009.
[4] WEI Xiao-qin, WU Hu-lin, ZHANG Lun-wu, et al. Natural Environmental Accelerated Aging Test Method of HTPB Propellant [J]. Equipment Environment Engineering, 2018, 15 (12): 104-108.
[5] Commission of Science, Technology and Industry for National Defense. Test method of propellant: GJB 770B-2005[S]. Beijing: Standardization Administration of China, 2005.
[6] HONG Dong-pao, Wang Ying-hua, GUAN Fei, et al. Storage life assessment for solid propellant based on generalized linear model[J]. Journal of Beijing University of Aeronautics and Astronautics, 2015, 41(4): 29-32.
[7] WANG Guo-qiang, SHI Ai-juan, DING Li, et al. Mechanical properties of HTPB propellant after thermal accelerated aging and its life prediction[J]. Chinese Journal of Explosives & Propellants, 2015, 38(1): 47-50.
[8] CAO Fu-qi, LIU Zhi-cheng, LI Xiao-huan. Research on accelerated aging test and storage life prediction of solid rocket motor charge[J]. Aero Weaponry, 2014 (4): 59-61.
[9] ZOU Si-si, Yan Cong, MA Cen-rui, et al. The dualistic linear regression model of HTPB propellant’s elongation under constant strain[J]. Journal of Northeastern University: Natural Science, 2010, 31(2): 261-264.
[10] GAO Da-yuan, He Bi, Liu Song-wei, et al. Discussion on limitations of the Arrhenius methodology [J]. Chinese Journal of Energetic Materials, 2006, 14(2): 132-135.