Effect of prestrain on storage life for HTPB coating in solid rocket motor

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Abstract. The prestrain thermal accelerated aging tests of HTPB coating at 0%, 3%, 6% and 9% levels were carried out. The variation of maximum elongation of HTPB coating at different aging stages was analyzed. The maximum elongation was selected as the performance characterization parameter, and the aging model of HTPB coating was established. According to the time-temperature equivalence principle, the time conversion relationship between prestrain thermal accelerated aging and effective storage at room temperature was obtained, and the storage life of HTPB coating at room temperature was predicted using this model. The results show that the predicted storage life of HTPB coating at room temperature is 18.64a, 18.08a, 9.24a and 7.44a, respectively, under the aging conditions with prestrains of 0, 3, 6, and 9%. The existence of prestrain will have a significant impact on the storage life of HTPB coating, which should be avoided in actual storage.

1. Introduction
As one of the most necessary components of solid rocket motor, the coating can make composite solid propellant grain firmly adhere to the insulation layer or motor case [1]. Nowadays, the majority of the coatings for solid rocket motors in China are HTPB coatings [1,2]. HTPB coating is continuously affected in storage period by the factors consist of the environment and the load. The deterioration of the microstructure and mechanical properties of HTPB coating will happen, which will reduce the storage life and cause unavoidable damage [3,4].

Lu [5] studied the mechanical properties of HTPB under stress and non-stress. They found that the storage life under 15% constant strain condition was shortened by about 4 years compared with that under non-stress condition. The HTPB and NEPE are two different types of propellants. Their research methods are universal and their change mechanism of performance is similar. Therefore, the performance of HTPB can be studied by referring to the results of NEPE propellant which have been reported already. Zhang [6] studied the changes of mechanical properties, gel properties and interfacial properties of NEPE propellant during storage under 20% constant strain. It indicated that the degradation mechanism of the binder matrix and the “desorption” of the interface were the main aging mechanisms. Zou [7] considered the effect of mechanical-thermal coupling on HTPB, and combined the characteristics of linear and exponential models, established a binary regression model, which was
applied to the prediction of natural storage elongation and life evaluation. Li [8] used the Kooij method to predict the storage life of samples at room temperature. The mechanical properties and storage life of HTPB coating are affected by the mechanical-thermal coupling factors in the storage process and there are few reports about the effect of prestrain on the mechanical properties and storage life of HTPB coating [9].

In our research, the thermal accelerated aging test under different prestrains was conducted. The maximum elongation was analyzed. The maximum elongation was selected as the characterization parameter, then the aging model for HTPB coating was built. The storage life of HTPB coating at room temperature was obtained using the time-temperature equivalence principle, and the influence of prestrain on the storage life was studied.

2. Materials and tests

2.1. Test Materials
The HTPB coating is shaped in the light of the QJ 916-85 [10], which is consist of HTPB, TDI, DOS, ZnO, SiO$_2$ and molecular sieve as shown in figure 1.

![Figure 1. Diagram of HTPB coating.](image)

2.2. Thermal accelerated aging test under prestrains
The temperature of the aging test was set to 70°C and the temperature fluctuation range was ±1°C. References [9,11] found that the max strain imposing on the coating is no more than 10%. Hence, as shown in figure 2. The HTPB coating was aging with the prestrians of 0, 3, 6, and 9%, respectively. The aging time was 3, 6, 9, 12, 15, 20, 30, and 40 days, respectively.
2.3. Maximum elongation test
The maximum elongation was tested using Instron 5982. The environment temperature was 25°C±2, and the test was conducted at the rate of 50 mm/min. The maximum elongation was recorded for different aging times.

3. Results and discussion

3.1. Test results of the maximum elongation
The maximum elongation test results are shown in figure 3.

Figure 3. The variation curves of maximum elongation.

With the aging time increasing, the maximum elongation rapidly decreased at first, and slowly decreased afterwards. During aging 0-15d, the increased cross-linking due to the effect of post-curing and oxidative cross-linking resulting in the maximum elongation decreased rapidly [12]. After aging 15 days, the post-curing effect was complete, and the influence of oxidative cross-linking was stronger than the influence of degradative chain scission to a small extent, hence, the maximum elongation decreased slowly [12]. Under the same aging time, with the prestrain getting larger, the maximum elongation became slower. This is because the molecular chain structure of HTPB coating was destroyed by different degrees of tension under the action of prestrains [13,14], which results in the maximum elongation decreasing with the increase of prestrain.

3.2. Modeling and solution
At present, the exponential model, the logarithmic model and the linear model are widely used to analyze the data of thermal accelerated aging test, and then to predict the service life under room temperature storage [15].

The exponential model:
\[ \varepsilon_m = \varepsilon_{m0} e^{-kt} \] (1)

The logarithmic model:
\[ \varepsilon_m = \varepsilon_{m0} + k \log t \] (2)

The linear model:
\[ \varepsilon_m = \varepsilon_{m0} + kt \] (3)

where \( \varepsilon_m \) is the maximum elongation of HTPB coating at a certain time of aging; \( k \) is the aging reaction...
rate constant; \( t \) the aging reaction time; \( \varepsilon_{m0} \) is the constant.

According to the results, the parameters of the three models were regressed by the Levenberg-Marquardt algorithm, and the correlation of three aging models was analyzed. The results of parameters fitting and correlation analysis are shown in table 1.

| Models         | Prestrain (%) | \( \varepsilon_{m0} \) | \( k \)     | \( R \)      | \( n \) |
|----------------|---------------|-------------------------|------------|-------------|-------|
| Exponential    | 0             | 407.69774               | 0.00951    | 0.84115     | 9     |
|                | 3             | 394.0449               | 0.00948    | 0.7186      | 9     |
|                | 6             | 381.05921              | 0.01072    | 0.70573     | 9     |
|                | 9             | 369.29366              | 0.01241    | 0.68246     | 9     |
| Logarithmic    | 0             | 447.10292              | -91.83545  | 0.94779     | 9     |
|                | 3             | 424.15427              | -83.01114  | 0.90547     | 9     |
|                | 6             | 399.95156              | -78.25575  | 0.96119     | 9     |
|                | 9             | 378.92535              | -76.65735  | 0.95338     | 9     |
| Linear         | 0             | 402.24038              | -3.0856    | 0.80241     | 9     |
|                | 3             | 388.11663              | -2.92578   | 0.67496     | 9     |
|                | 6             | 374.05601              | -3.11107   | 0.6595      | 9     |
|                | 9             | 360.9093              | -3.3759    | 0.63626     | 9     |

Note: \( R \) is the correlation coefficient, \( n \) is the sample number.

It can be seen from table 1 that the logarithmic model has the highest fitting correlation coefficient, especially under the condition of adding prestrains, the correlation coefficient of aging model is still greater than 0.9000. Therefore, the logarithmic model was selected as the aging model to describe the maximum elongation of HTPB coating.

3.3. The effect of prestrain on storage life

According to the time-temperature equivalence principle [16], the equivalent conversion relationship between thermal accelerated aging time and storage time at room temperature is as follows:

\[
\tau_{25}=365^4 \cdot \tau_T \cdot \gamma^{\frac{T-25}{10}}
\]

where \( \tau_{25} \) is the predicted life at 25°C, \( \tau_T \) is the aging time, d; \( T \) is the aging temperature, °C; \( \gamma \) is the temperature coefficient. According to Van Hough's law [17], the temperature coefficient can take from 2 to 3. This paper mainly studies the effect of prestrain on storage life, so the temperature coefficient was taken as 2.

Taking the maximum elongation reduction of 50% as failure criterion [18]. The storage life at 70°C and storage at room temperature can be obtained from equations (2) and (4), as shown in table 2 and figure 4.

| Temperature (°C) | Prestrain (%) | Decreased range, % |
|------------------|---------------|--------------------|
|                  | 75            | 25                 |                   |
| 0                | 300.6097 d    | 18.64 a            | —                 |
| 3                | 291.7217 d    | 18.08 a            | 3.00              |
| 6                | 149.076 d     | 9.24 a             | 50.43             |
| 9                | 120.023 d     | 7.44 a             | 60.09             |
As can be seen from table 2 and figure 4, the storage life of HTPB coating showed a downward trend. Due to the influence of the prestrain, the polymer chains expand from the curling state, the polymer chains reorient, the orientation of the molecular chains increases in the direction of force, and the chain scission effect of the coating was strengthened, which will lead to the deterioration of material properties. The higher the prestrain, the more serious the damage to the molecular structure, the worse the material performance deteriorates. The deterioration of properties will shorten the storage life of the coating [19,20]. The storage life of HTPB coating decreased slightly (3.00%) with 3% prestrain. When the prestrain increased to 6%, the storage life decreased significantly (50.43%). This indicated that the existence of prestrain will significantly affect the storage life of HTPB coating. In the actual storage process, strain, especially large strain, should be avoided as far as possible.

4. Conclusions
The existence of prestrain will have a significant impact on the storage life of HTPB coating. In order to study the effect of prestrain on storage life for HTPB coating, this work was carried out and the conclusions were shown below:

- The thermal accelerated aging tests under prestrains of 0, 3, 6, and 9% were conducted, and the variation of maximum elongation was analyzed. The maximum elongation firstly decreased with the aging time. At the same aging time, with the prestrain getting larger, the maximum elongation became lower;
- The maximum elongation was selected as the performance characterization parameter and a logarithmic aging model of HTPB coating was built. In the light of the time-temperature equivalence principle, the storage life of HTPB coating under room temperature storage was predicted effectively;
- The prestrain has a major influence on the storage life. With the aging prestrains of 0, 3, 6, and 9%, the predicted results of HTPB coating storage life at room temperature were 18.64a, 18.08a, 9.24a and 7.44a, respectively. Compared with a zero prestrain, the storage life of HTPB coating decreased by 3.00, 50.43, and 60.09%, respectively. The higher the prestrain, the shorter the storage life. In the actual storage process, pre-strains, especially large ones, should be avoided as far as possible.

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