Research Article

Comprehensive Evaluation of the Accelerated Aging Law of NEPE Propellants

Yulong Liang, Mi Zhang, Hui Ren , and Qingjie Jiao

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China

Correspondence should be addressed to Hui Ren; renhui@bit.edu.cn

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In order to study the accelerated aging law of nitrate ester plasticized polyether (NEPE) propellants, the mechanical properties, weight loss, adhesive network structure fracture, and stability of NEPE propellants during storage were analyzed. The results show that the maximum tensile strength σ_m shows good change law with the increase of storage time, and the failure of NEPE propellants is mainly strength failure. The content of the stabilizer decreased with the increase of storage time. With the prolongation of storage time, the weight loss ratio increases gradually with good regularity. The decomposition of the components in the propellant leads to the degradation of the polyethylene glycol (PEG) network structure. The thermal decomposition of the nitrate plasticizer in NEPE propellants will occur, and the products will cause the adhesive network structure to decompose and break the chain, leading to the destruction of the matrix structure. The thermal decomposition of the propellant has temperature-increasing rate dependency.

1. Introduction

Solid rocket engines are important defense products, and the health status has a critical impact on weapon reliability. To a large extent, the storage life of solid rocket engines depends on the storage properties of solid propellants, including physical and chemical properties, internal ballistic performance, and structural integrity [1]. However, the solid propellant is an unstable material that will cause physical and chemical aging during long-term storage [2]. Physical aging refers to changes in the physical properties of solid propellants during the storage periods, such as moisture absorption, dehumidification between the oxidant and the binder interface, solvent vitalization, debonding between the propellant and the liner, cracks and voids caused by stress or strain, and other changes in physical properties. Chemical aging refers to the change in properties of solid propellants caused by chemical changes during processing, storage, and use, such as thermal decomposition, hydrolysis, degradation, decomposition of oxidants, oxidative crosslinking, and degradation of adhesives. The chemical changes caused by

the interaction of various components of the propellant or reaction with the air are irreversible, and the rate of change varies with different storage conditions. Therefore, the study of the solid propellant aging mechanism is the basis of its storage life assessment and an important issue in the life prediction of solid rocket engines [3–5].

NEPE combines the advantages of the double-base propellant and composite propellant. It is a new type of propellant with excellent energy performance and mechanical properties at present and represents the development direction of high-energy solid propellants [6–8]. However, in the storage process, this type of propellant is prone to complex aging phenomena, causing engine failure and leading to safety risks and economic losses [9–11]. Therefore, it is necessary to carry out an in-depth analysis of the aging performance characteristics of NEPE propellants to provide a theoretical basis for the next step in finding effective antiaging measures. In the article, we analyze the storage performance of NEPE solid propellants, explore the accelerated aging rules of NEPE propellants, and study their health detection technology.

2. Materials and Characterization

The NEPE propellant used in the experiment adopts the general PEG/N100 system, and the propellant uses mixed nitrate (a mixture of NG and BTTN) as a plasticizer. First, propellant slurry is cast into a certain size of the propellant sample, and then a certain shape and size of the sample are prepared. Propellant mechanical property test specimens are prepared according to type B specimens in GJB770B-2005 method 413.1, "maximum tensile strength, breaking strength, maximum elongation, and breaking elongation unidirectional tension method," and the accelerated storage test specimens are a 120 mm × 120 mm × 10 mm sheet sample. Propellant adhesive test pieces were prepared in proportion with PEG, N100, and mixed nitrate.

The DU288 oil bath oven of Shanghai Experimental Instrument Factory Co., Ltd., was used to carry out the accelerated storage test, and the oven temperature uniformity was $\leq 2^{\circ}\text{C}$. The Instron 5567 tensile machine made in the United States was used to test the maximum tensile strength σ_m and maximum elongation ϵ_m of the propellant in different aging processes at 25°C . The test method follows GJB770B-2005 method 413.1, and the stretching rate is 100 mm/min. The thermoelectric company Nicolet 6700 Fourier-transform infrared spectrometer was used to analyze the functional group changes during the storage of the adhesive system. The DSC204F1 differential thermal scanning calorimeter of the German NETZSH company was used to analyze the thermal decomposition performance of the sample, and the heating rate was $5^{\circ}\text{C}/\text{min}$, $10^{\circ}\text{C}/\text{min}$, $15^{\circ}\text{C}/\text{min}$, and $20^{\circ}\text{C}/\text{min}$. The Mettler Toledo XP404S weighing balance was used to test the weightlessness of samples during the aging process. The FGD2-B- NO_x nitrogen oxide analyzer was used to test the NO_x gas released from the sample, and the FGD2-B- CO_2 carbon dioxide detector was used to test CO_2 gas.

3. Results and Discussion

3.1. Mechanical Properties of the NEPE Propellant during Accelerated Storage. NEPE propellant accelerates aging at 55°C , 60°C , 65°C , and 70°C , and the changes in the maximum tensile strength σ_m and the maximum elongation ϵ_m with the aging time during accelerated storage are tracked and measured, which are shown in Figure 1. Figure 2 shows the change of the stabilizer content in the propellant with aging time.

As shown in Figure 1, in the process of thermally accelerated aging at different temperatures, the maximum tensile strength value fluctuates within a small range in the initial stage of aging and decreases rapidly in the later stage. And as the aging temperature increased, the time for the maximum tensile strength value to decrease shortened. Figure 2 shows that stabilizers are continuously consumed as the aging time increases. Comparing the maximum tensile strength and the stabilizer content change chart, it can be seen that the maximum tensile strength fluctuates within a small range before the stabilizer is completely consumed, but the maximum tensile strength begins to reduce rapidly after

the stabilizer is consumed. It is speculated that the change law of the maximum tensile strength is related to the stabilizer content in the propellant. The initial stage is that the stabilizer is consumed by the nitrate decomposition products. In this stage, the stabilizer continuously reacts with nitrogen oxides decomposed by nitrate to form a nitroso product, which inhibits the decomposition of nitrate. When the stabilizer is consumed, nitrate decomposition products act on nitrate for the autocatalytic reaction, and the mechanical properties decrease rapidly.

At the initial stage, there is an obvious rising process of ϵ_m , which is mainly caused by the physical tensile action of constant strain. The reason may be that the polymer chain of the NEPE propellant binder matrix is degraded, and the chain scission effect is strengthened under the action of constant strain, which improves the elongation of the propellant. Under the action of constant strain, the polymer chains are unfolded from the collapsed state, the chains are oriented and rearranged, and the molecular chains are oriented more in the direction of the force, which increases the elongation of the propellant to a certain extent. In the later stage of aging, the influence of aging of the adhesive matrix and the dehumidification of the interface between the adhesive matrix and the solid filler is gradually significant. With the occurrence of the dehumidification phenomenon, the physical or chemical adsorption force between the dispersed phase and the continuous phase decreases, which weakens the stress transmission in the entire system and causes the maximum elongation of the propellant to decrease.

Based on the changes in the maximum tensile strength and the maximum elongation of NEPE propellants, it is shown that the failure of NEPE propellants is mainly strength failure.

Figure 3 is the state diagram of the NEPE propellant after accelerated storage. It indicated that the matrix structure became soft and bulging, and pores were present during the later accelerated storage period of the NEPE propellant. The appearance of pores indicates the emergence of gas inside the propellant. The polymer chain of the propellant will undergo a chain scission reaction. Under the condition of accelerated aging, the chemical reaction rate of chain scission will increase and be accompanied by gas precipitation. Then, the pores of the propellant matrix will appear.

3.2. Weight Loss in the Process of Accelerated Storage. The thermal weight loss during accelerated storage of the NEPE propellant and hydroxyl-terminated polybutadiene (HTPB) propellant is compared, which is shown in Figure 4.

NEPE propellant is aged by storing at 70°C , and its weight loss rate gradually increased with the extension of storage time and reached about 10% when stored for 140 days (3360 h), which has not yet reached the limit. It indicates that the NEPE propellant will undergo a significant decomposition reaction when stored at 70°C , but for the HTPB propellant, the value of weight loss is almost constant. For the thermal parameters for the NEPE propellant, the regularity between weight loss rate and storage time is great,

FIGURE 1: The change rule of σ_m and ϵ_m of NEPE at different storage temperatures.

FIGURE 2: The content of the stabilizer at different storage temperatures.

FIGURE 3: The state diagram of NEPE after accelerated storage.

and the detection of the weight loss rate is easy to implement. Therefore, the weight loss rate can be used as a health monitoring index for similar propellants.

3.3. Adhesive Network Structure Fracture Test. Two groups of NEPE propellant adhesive samples were selected for the 80°C storage test. One group is PEG adhesive films. The other group is composed of PEG adhesive films and NEPE propellants. Figure 5 shows the PEG adhesive film before and after storage. Figure 6 exhibits the state of storage of the NEPE propellant with the PEG adhesive network structure before and after storage.

FIGURE 4: Comparison of the thermal weight loss of the NEPE propellant and hydroxyl-terminated polybutadiene propellant during accelerated storage at 70°C.

FIGURE 5: The images of the PEG adhesive film before (a) and after (b) storage.

FIGURE 6: The images of storage of the NEPE propellant with the PEG adhesive network structure: before (a) and after (b).

TABLE 1: Gas release during accelerated aging of the NEPE propellant.

50°C			60°C			70°C		
Time of storage (d)	Gas release		Time of storage (d)	Gas release		Time of storage (d)	Gas release	
	NO _x (ppm)	CO ₂ (%)		NO _x (ppm)	CO ₂ (%)		NO _x (ppm)	CO ₂ (%)
23	1.4	0.9	20	1.3	1.7	17	7.8	3.6
53	2.8	1.0	34	1.5	2.4	25	5.7	4.9
105	3.9	0.9	48	26	5.9	42	280	25.9
124	23	2.3	72	346	7.6	48	842	32
158	89	5.6	136	1508	15.7	52	1216	43
206	212	7.8	183	3860	23.7	62	5000	51

It can be seen from Figure 5 that matrix color turns yellow, and the structure has not changed after the single film is stored thermally. Figure 6 shows that the film and propellant are stored together for thermal storage, the PEG adhesive undergoes a significant degradation reaction, and the adhesive network structure is damaged. After degradation, the adhesive loses its original mechanical strength. The results indicate that the decomposition of components in the propellant leads to the degradation of the PEG network structure during the thermal storage of the NEPE propellant.

3.4. Changes of NEPE Propellant Aging and Degradation Release Gas. In the NEPE propellant accelerated storage experiment, the amount of gas in the sealed bag is regularly detected, and the result is shown in Table 1. Figure 7 exhibits the variation of NO_x and CO₂ release with storage time at different temperatures.

As shown in Figure 7, the gas release rate of the propellant is faster with a higher temperature. At 70°C, NO_x and CO₂ released by the NEPE propellant increased exponentially and began to soften after around 60 days. The content is the maximum value to maintain the structural integrity of the propellant. At 60°C, the NEPE propellant did not soften after more than 180 days of storage. At this time, the amount of NO_x released was 3860 ppm, and the amount of CO₂ released was 23.7%. The amount of gas released by the NEPE propellant slowly increased with the extension of storage time at 50°C. The NO_x gas detected at 206 days was 212 ppm, and the amount of CO₂ was 7.8%.

3.5. The Degradation Reaction of the NEPE Propellant. NEPE propellant decomposition mainly includes nitrate decomposition and polyurethane decomposition. Combined with the above experiments, the decomposition reaction process of the NEPE propellant during accelerated storage can be speculated.

The nitrate decomposition reaction process is shown as follows:

The polyurethane adhesive of the NEPE propellant contains the ether group and urethane group and can react under the action of water:

The degradation of the NEPE propellant during storage is caused by the decomposition of nitrate. H₂O and NO_x radicals are generated during the decomposition of nitrate, and the free radicals promote the continued decomposition of nitrate. H₂O is the main factor that promotes the decomposition of adhesive polyurethane, which leads to the chain breakage of the adhesive polymer and the damaged matrix structure of the propellant. When the decomposition reaction cannot be inhibited by the stabilizer, the decomposition reaction will continue to decompose to a certain degree, the polymer chain in the adhesive network structure is generally broken, and the propellant is transformed from a softened state into pulp. Figure 8 is the sketch of structural failure caused by aging and decomposition of the NEPE propellant.

The thermal decomposition of the nitrate plasticizer in NEPE will cause the decomposition of the adhesive network structure to cause chain breakage, resulting in damage to the matrix structure. It can be known from the decomposition process of propellants that NO_x is mainly produced by the decomposition of nitrate, and CO₂ is produced by the decomposition of nitrate and binder. Therefore, NO_x is used as a characteristic gas for the health characterization of propellants.

3.6. Thermal Decomposition of NEPE Propellants. TGA/DSC was used to characterize the thermal behavior of NEPE propellants at different heating rates. The results are shown in Figure 9. It demonstrates that the thermal decomposition of the propellant depends on the temperature-raising rate. As the heating rate increases, the temperature of the first decomposition peak increased, and the second decomposition peak showed almost inconspicuous change. The first decomposition peak of the propellant on DSC is a severe exothermic peak, which is the decomposition of some plasticizers (such as NG and BTTN) with HMX participation. The TG curve shows that the weight loss rates under different heating rates are about 16%, 23%, 28%, and 32% in

FIGURE 7: Variation of NO_x and CO₂ release with storage time at different temperatures.

FIGURE 8: The sketch of structural failure caused by aging and decomposition of NEPE.

FIGURE 9: DSC and TG curves of NEPE at different heating rates

the first stage of decomposition. This illustrates that the thermal decomposition of mixed nitrate is affected by the heating rate. The endothermic peak at 237.9°C is the crystal transformation peak of AP. The second exothermic peak is mainly the decomposition of the binder, and the weight loss rates under different heating rates are about 42%. Therefore, the decomposition of the binder and heating rate are irrelevant.

4. Conclusion

In this work, the mechanical properties, changes in the components, weight loss, adhesive network structure fracture test, degradation reaction, and thermal decomposition of NEPE were researched in the process of accelerated storage. At different storage temperatures, as the storage time prolongs, the maximum tensile strength, maximum elongation, stabilizer content, mixed nitrate content, weight loss rate, and other parameters all show great variation rules, which can be used as propellant storage health monitoring indicators. The decomposition of the components in the propellant leads to the degradation of the PEG network structure. The thermal decomposition of the nitrate plasticizer in NEPE propellants will cause the decomposition of the adhesive network structure, which leads to chain breakage, resulting in damage to the matrix structure. The degradation of the NEPE propellant is caused by the decomposition of nitrate, and NO_x is mainly produced by the decomposition of nitrate. NO_x can be used as a characteristic gas for the health characterization of the propellant.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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