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Research on Solid Propellant Wet-Heat Aging Mechanism and Aging Test Characterization Methods

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ABSTRACT

Solid propellants are critical in aerospace and military applications. HTPB solid propellants are widely used because of their excellent performance, but hot and humid environments have a significant impact on their performance. This paper reviews the research progress of HTPB solid propellant wet heat aging mechanism and aging performance test characterization method. With respect to the moisture-heat aging mechanism, chemical aging is manifested by polymer chain breakage and reorganization, and physical aging is manifested by the migration of plasticizers leading to microstructural instability; In the aging test characterization method, there are macro test and fine test. The current study suffers from homogenization of method application, little qualitative analysis, incomplete exploration of aging mechanisms and poor accuracy of life prediction models. In the future, new anti-aging additives should be developed and combined with artificial intelligence to optimize the aging prediction model.

KEYWORDS

HTPB solid propellant; Aging mechanism; Experimental characterization methods

1. INTRODUCTION

Solid propellants are indispensable in aerospace and military fields, It's the heart of the propulsion system for rockets, missiles, and other weapons, Its performance directly affects the progress of space exploration and the security of national defense.Solid propellants are used in a wide range of applications, thanks to their high energy density, ease of storage and fast response time,Solid propellants become the preferred option for propulsion systems. Therefore, solid propellant research and development has always been a top priority in the development of space and military science and technology in various countries.

In the vast system of solid propellants, there are a variety of types with their own individual characteristics. HTPB solid propellant has established itself as a widely used propellant in the current propellant field due to its excellent mechanical properties, good processability and high energy characteristics [1]. Zhou Dongmu et al [2] pointed out that the performance of solid propellants greatly affects the storage life of solid rocket motors, especially the aging mechanism of propellants under constant strain conditions. Research on it is of great significance to improve the accuracy of life prediction and promote engineering applications.

In practice, HTPB solid propellant encounters a major key obstacle, namely the extremely significant impact of hot and humid environments on its performance. Under the action of hot and humid environment, it will lead to the decline of mechanical properties of propellant, the deterioration of

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interfacial bonding performance, and even cause the aging phenomenon, which will not only shorten the storage life of propellant, but also pose a threat to the safety of its use. Qin Pengju et al [3] showed that the maximum elongation at atmospheric pressure after propellant aging obeys a linear relationship. The performance degradation of HTPB propellants is even more critical in high temperature and high humidity coastal areas or tropical climates. Zhang Xiaojun et al [4] pointed out that the aging process of HTPB propellant in hot and humid environment can be subdivided into three stages. In the first stage, hygroscopic phenomenon is the dominant factor; while in the second stage, its aging process is closely related to the level of stress in the hot and humid environment. Zhang Lei et al [5] proposed that the inclusion of temperature and humidity factors in the propellant aging model is of great significance, which can make the prediction results closer to the actual propellant life in the engine, and significantly improve the accuracy of life prediction. Zhang Xudong et al [6] pointed out that wet aging deteriorates the mechanical properties of HTPB propellant, and that the relative humidity and temperature work together to make the relative tensile strength decrease faster and larger.

In view of the important position of HTPB solid propellant in aerospace and military fields and the significant influence of humid and hot environments on its performance, it is of great theoretical significance and practical application value to carry out related research. By systematically investigating the aging mechanism, performance degradation characteristics and protection methods of HTPB propellant under high temperature and high humidity conditions. On the one hand, it can provide scientific basis for propellant formula improvement and process upgrading, and enhance the intrinsic quality of propellant; on the other hand, it can provide technical support for propellant in storage, transportation, and use, so as to guarantee the long-term and stable operation of the weapon in an all-round way, and to ensure the safety of use.

2. PROGRESS OF HTPB SOLID PROPELLANT HYGROTHERMAL AGING MECHANISM RESEARCH

The key to solving the mechanism- and characterization-related problems lies in the aging mechanism of solid propellants, figuring out the influencing factors in the aging process and how these factors play a role in the life assessment. Huo Wenlong et al [7] pointed out that the accelerated aging process of solid propellants is the result of the joint action of factors such as external environmental factors and the nature of internal formulations, and these factors have a significant impact on their storage expiration date. Yang Gen et al [8] argued that solid propellant aging in hot and humid environments can significantly change its own properties, which in turn interferes with the accurate assessment of propellant lifetime. They emphasized that an in-depth analysis of the aging mechanism and dynamics is crucial for optimizing the aging assessment method, which can provide theoretical support for extending the propellant life. In hot and humid environments, HTPB solid propellant aging is accelerated and the key factors are the moisture and temperature in it. Zhang Xiaojun et al. [4] suggested that HTPB propellant would be decomposed, degraded and migrated in the process of humid-thermal aging, and the phenomenon of “crystal precipitation” would also occur. Humidity conditions affect the hygroscopicity, decomposition and migration of propellants, and these effects vary under different humidity conditions. The increase in temperature accelerates the chemical changes, ultimately making it possible to recover the physically aged properties of the propellant, but difficult to return to the initial state of the chemically aged properties.

Chemical aging is mainly characterized by the breakage and reorganization of polymer chains, Xinyuan Wang et al [9] showed that during the accelerated aging process of HTPB propellant, the changes in the concentration of hydroxyl (-OH) and carbonyl (C=O) as well as the oxidative cross-linking process triggered by ammonium ions (NH4+) can be effectively tracked by infrared spectroscopy. The dynamic evolution of these chemical reactions directly leads to a reduction in the ductility of the propellant material, and its maximum elongation decay phenomenon shows a

significant correlation with the spectral data. The research results verify the technical feasibility of infrared spectroscopy for quantitatively assessing the aging behavior of solid propellants. Sun Haitao et al [10] proposed that the chemical degradation reaction and component migration and diffusion behavior of solid rocket propellant in the aging process will induce the generation of microcracks in the interface region between the matrix material and the reinforcing filler. This interfacial damage mechanism not only causes the degradation of mechanical properties such as reduction in mechanical strength and decline in elastic modulus of the material, but also significantly improves the sensitivity of the propellant system to external stimuli, which increases the probability of material failure and the risk of accidental ignition. Pei Liguan et al [11] pointed out that the aging performance of composite solid propellants can be comprehensively analyzed by carrying out a comprehensive study from the three dimensions of traditional aging characteristics, chemical aging characteristics, and storage life prediction. Identifying aging characteristics such as mechanics, images, and component content, and using analysis tools such as chemical functional groups, molecular simulation, and gas content can provide an in-depth understanding of the propellant aging mechanism and significantly improve the accuracy of the life prediction model.

Physical aging is mainly manifested as microstructural destabilization. Under the combined effect of high temperature and high humidity, the plasticizer DOA diffuses and migrates in the viscoelastic matrix, and is enriched on the surface of the material. This material redistribution allows the matrix to become densely cross-linked, which is macroscopically reflected in a significant increase in the modulus of elasticity. Scanning electron microscopy reveals micron-scale interfacial defects on the surface of the aged specimen, like stress cracks and dehumidified pores, and these interfacial changes lead to a deterioration of the material's resistance to deformation and an increase in the risk of failure [12].

Tang Guojin et al [13] innovatively combined accelerated aging test data with stochastic finite element model to show the degradation of mechanical properties of solid propellants with storage time by numerical simulation, and constructed a probabilistic prediction model. This study quantitatively evaluates the structural reliability of a certain type of propellant with different service lives, realizes the statistical prediction of service life, and provides theoretical support for the life assessment and life extension decision of solid rocket motors, with significant engineering application value. Chen Xuewen et al. [14] focused on solid rocket motor propellant aging research, constructed the chemical kinetic aging constitutive equation, and established a storage life prediction model. Based on the failure criterion to determine the performance degradation threshold, the experiment shows that the maximum elongation of propellant in natural storage for 10 years decreased by 27.3%, and the residual performance still meets the standard. Scholars at home and abroad have developed a variety of aging prediction models based on macro-mechanical parameters, and the prediction is stable in engineering. However, fine-scale aging models for microstructural evolution need to be improved in terms of prediction accuracy and applicability due to insufficient microscopic characterization and multiscale correlation models.

3. ADVANCESIN CHARACTERIZATION METHODS FOR MOISTURE-HEAT AGING PERFORMANCE TESTS

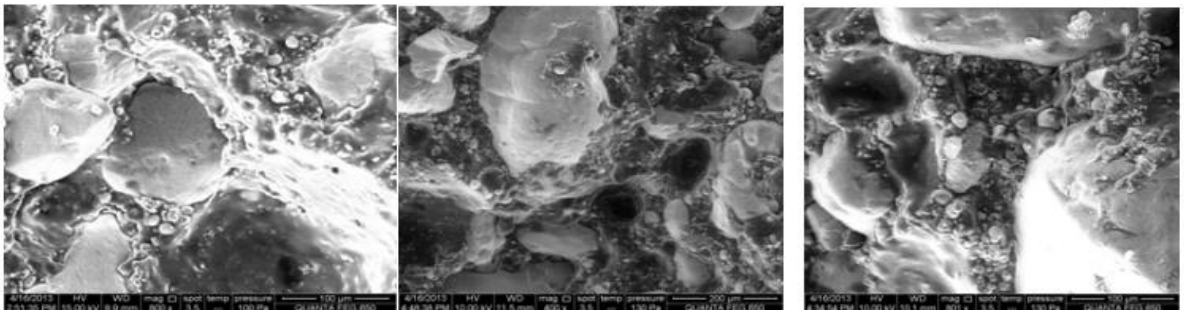
3.1. Macro-Test

Macroscopic methods for testing the aging properties of HTPB propellants include tensile testing, dynamic thermo-mechanical analysis, differential sweep calorimetry, and thermogravimetric analysis. The tensile test is conducted under preset temperature and tensile rate conditions by continuously applying axial tensile load until the specimen breaks, and the load-displacement change curve is synchronously recorded by using a data acquisition system to ultimately determine and analyze the ultimate tensile strength, elongation at break, and other key mechanical property parameters of the

solid propellant. PaiPeng et al [15] found that the mechanical properties of HTPB propellant under tensile and compressive loading were significantly different by constant velocity tensile and compressive tests and cross-section SEM scanning, and the tensile strength was much smaller than the compressive strength, and this difference was mainly affected by the matrix, and the particles had more obvious effects on the mechanical properties in compression.Based on this, the tensile-compressive integrated nonlinear eigenstructure model is realized in simulation calculations, and the theoretical, simulation and experimental results are in high agreement. He Tieshan et al [16] pointed out that humidity significantly affects the unidirectional tensile mechanical properties of HTPB propellant, with a small effect at low humidity, and high humidity causes a rapid decline in mechanical properties, which can be partially restored by drying treatment after moisture absorption. The data from the study of Li Muchen et al [17] showed that during the aging stage of the material, the tensile strength at room temperature (20°C) is positively correlated with the surface hardness of the material, and the tensile strength at high and low temperatures (60°C, -40°C).

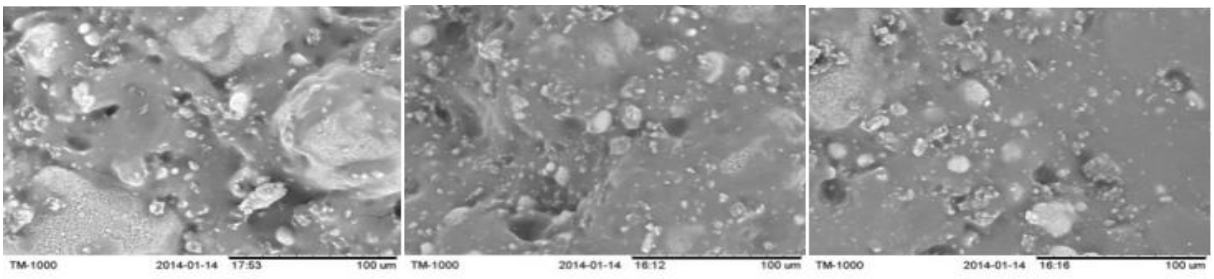
3.2. Fine View Test

Macroscopic methods for testing the aging properties of HTPB propellants include the use of scanning electron microscopy (SEM), transmission electron microscopy (TEM), e.g., infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR).In the study of Xinyuan Wang et al [9], the accelerated aging process of HTPB propellant was analyzed by infrared spectroscopy, which verified the application value of the method in quantitatively evaluating the aging performance of the propellant. Zeng A-Ya et al [18] carried out experiments on HTPB propellant after moisture-heat aging with the help of scanning electron microscope (SEM) and micro dynamic tensile device. Observing the microscopic morphology by SEM, it was found that the hot and humid environment leads to changes in the interface between the particles inside the propellant and the substrate, such as the phenomenon of interfacial debonding; Combined with the micro dynamic tensile device to analyze the fracture behavior, it further reveals how the microstructural evolution triggered by hygrothermal aging affects the macroscopic mechanical properties of the propellant, and establishes an intrinsic link between the two. Zeng Yi et al [19] based on the heat-force coupling effect study, revealing that the coupling effect on the HTPB propellant microscopic damage of the significant role in promoting the specific performance of the matrix mechanical properties of the deterioration of the phenomenon of particle dehumidification and thermal degradation accelerated, and confirmed that the aging temperature and the degree of the microscopic damage is positively correlated with the law of the degree of aging temperature increase. In addition, the study clarified that a reasonable setting of the number of termination loadings is a critical control parameter for the accurate determination of fine-scale damage sprouting.



a) 3%constant strain b) 6%constant strain c) 9%constant strain

Figure 1. SEM image of accelerated aging at 75℃ for 18 days



a) 3%constant strain b) 6%constant strain c) 9%constant strain

Figure 2. SEM of accelerated aging at 60℃ for 102 days

Table 1. Macroscopic, fine-scale test characterization methods

Research -scale	characterization method	research purpose
Macro-scale	Tensile test	By setting a specific tensile rate and tensile temperature, a standard tensile specimen is allowed to be pulled to fracture under the constant action of a static axial tensile force.
	Dynamic thermo-mechanical analysis (DMA)	Measurement of mechanical properties of propellants as a function of time. temperature, and frequency.
	Differential scanning calorimetry (DSC)	Qualitative and quantitative analysis of the magnitude of thermal effects during reactions
Micro-scale	Scanning electron microscope (SEM)	Observation of changes in propellant structure
	Fourier transform infrared (FTIR) spectrum	Provides detailed information on chemical bonds and functional groups in propellant molecules, identifies and detects aging indicators.
	Chromatography	composite solid propellants. There are mainly gas chromatography and liquid chromatography.
	Nuclear magnetic resonance spectroscopy (NMR)	Used to study the microstructure of propellants and the type and distribution of hydroxyl groups

Zhang Pan et al [20] indicated that the optimization of the experimental method for propellant material aging was achieved by investigating the macro- and microscopic aging characteristics and their correlation. This optimization has led to significant progress in the study of the aging properties of hydroxybutyl (HTPB) propellants, which will play a positive role in promoting the future development trend in this field.

4. SUMMARY

Solid propellant aging is subject to a combination of hot and humid environments, and coupled chemical-physical mechanisms. Chemical aging is dominated by polymer chain breakage and reorganization, which triggers the decay of mechanical properties, while physical aging is manifested by the migration of plasticizers leading to microstructural destabilization. The experimental research method establishes a tensile-compressive nonlinear ontological model, realizes high-precision simulation prediction of mechanical properties, clarifies the dominant mechanism of microstructures such as interfacial defects on macroscopic mechanical degradation, and puts forward the interface optimization strategy. Currently, solid propellant aging research has an obvious homogenization problem in the application of methods. Most of the studies focus on quantitative analysis, and the use

of qualitative analysis is relatively scarce. In the data analysis segment, traditional statistical methods dominate, and when faced with complex data, these methods are difficult to meet the demand, and the analytical ability is stretched. In addition, there are problems of insufficiently comprehensive exploration of the aging mechanism and poor accuracy of the life prediction model, which need to be improved. In the future, it should also be developed towards the development of new anti-aging additives, combined with artificial intelligence to optimize the aging prediction model.

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