Aging Properties of Nitrile Rubber in Medium under High-Low Cyclic Temperature Environment

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Abstract. To obtain the aging mechanism of a certain kind of missile sealing nitrile rubber material under high and low-temperature cycle conditions, the nitrile rubber sealing ring was subjected to the accelerated aging test of high and low temperature circulating oil medium. The changes of compression set, mechanical properties, microstructure, molecular structure and dynamic mechanical properties under the condition of temperature-changing oil medium were studied. The dissociation energy of several important chemical bonds of nitrile rubber molecules was calculated. The test results show that the maximum tensile strength and elongation at break of special nitrile rubbers decrease with the increase of the number of cycles, and the compression set rate of nitrile rubber samples stored in oil medium increases gradually in the early stage of aging. Large, slightly restored in the late stage of aging, as the aging time increases, the side groups of the nitrile rubber molecules decompose and the main chain flexibility increases.

1. Introduction
At present, a large amount of rubber material is used as a sealing material in the naval anti-ship missile power system. In recent years, many accidents have been continuously caused by the failure of the sealing structure among the naval forces, such as fuel leakage and dynamic failure. These accidents lead to serious safety hazards to the missile fuel system. Therefore, the failure of the seal structure has become one of the main failure modes of the missile power system. Nitrile rubber is obtained by emulsion copolymerization of acrylonitrile and butadiene. Because it contains the polar substance—acrylonitrile, it has excellent resistance to solvents such as non-polarity or weak polarity oils. In general, the higher the acrylonitrile content, the higher the performance of the medium with high-temperature resistance and oil resistance. Because of its good oil and high-temperature resistance, it has been widely used in the sealing device of the pilot engine air intake pipe and one-way valve.[1]

In recent years, a lot of researches on the aging behavior of nitrile rubber oil-resistant medium have been carried out at home and abroad. Ji Lianzhong[2] and Wang Dengxia[3] analyzed the aging properties of different types of nitrile rubber stored in different regions through experiments. The experimental results show that the compression set rate of nitrile rubber is higher in areas with higher annual average temperature. The maximum tensile strength changes were faster than the average annual temperature. Wang Dengxia summarized the performance variation of five years of nitrile rubber in five regions and believed that hydrogenated nitrile rubber has a service life of about 2 to 6 years under five different conditions. Xiong Ying[4] and Garbarczyk[5] studied the aging behavior of
nitrile rubber in hot air aging condition. It is found that stress has a great influence on the properties of nitrile rubber. Under the influence of stress, the storage life of the nitrile rubber is reduced by 50%. At this time, the molecular chain of the rubber molecule is oriented and deformed, and the length and angle of the molecular chain are changed. Further, the activation energy of fracture is lowered, and the lifetime is reduced. Garbarczyk found that the molecular weight of the nitrile rubber increased, and the molecular chain cross-linked as the aging time prolonged by NMR test of the nitrile rubber after hot oxygen aging for a certain period. Wang Huiming[6] and Zhang Fengling[7] conducted oil-resistant medium experiments on different grades of nitrile rubber used in the aviation field and compared the oil resistance of different grades of nitrile rubber. The experimental results show that the fuel immersion causes the rubber to swell for a certain period, and the mechanical properties such as tensile strength and elongation of the nitrile rubber also change greatly with the increase of the immersion time. Wang Huiming also used the BP neural network model to predict the stator wear under different parameters.

These research contents focus on the performance change of nitrile rubber under high-temperature medium. In fact, as a seal for missiles, the working environment temperature of the seal often changes periodically with time, which leads to the change of aging properties of nitrile rubber medium in previous studies. The law no longer applies. In this paper, the aging test of high temperature and the low-temperature cycle of nitrile rubber is mainly carried out. Based on the dynamic and static mechanical properties test and the results of Fourier transform infrared spectroscopy, combined with the simulation calculation of the chemical bond dissociation energy of nitrile rubber, the oil under high and low-temperature cycle conditions is summarized. The change rule of nitrile rubber properties stored in the medium and its aging mechanism.

2. Experiment

2.1. Equipment and materials
The experiment used special nitrile rubber produced by Solvay (Shanghai) Co., Ltd., and RP-3 aviation kerosene.

The sample type of mechanical property test is the type 1 sample specified in GB/T 528-2009. The test instrument is the CMT4203 universal test machine produced by MTS Industrial, the tensile rate is 100mm/min, and the test temperature is 23±2 °C; The sample of the compression set test was prepared according to the A-type cylindrical sample specified in GB/T 7759-1996, and the height of the limiter was set to 9.12 mm, and the compression ratio was 25%. The infrared spectrometer adopts Nicolet iS50 of Nico, the wavelength range is 500~4000, the resolution is 4; the scanning electron microscope choose HITACHIS-4800, the scanning position is the section of the tensile test sample; the Dynamic mechanical performance analyzer is produced by PE company. Dynamic mechanical property test was carried out at a frequency of 1 Hz, a heating rate of 3 °C/min, and test temperature of -90 °C to 60 °C.

2.2. Method of the aging test under high-low cyclic temperature
The nitrile rubber resistant medium aging test is carried out according to GB/T 1960-2010 Vulcanized rubber or thermoplastic rubber liquid resistance test method and GJB 150.5-86 Military equipment environmental test method, The temperature range is -40 °C ~ 80 °C. In combination with GJB 1172.3-1991 Military Extremes for Military Equipment, Surface Air Humidity, the parameters of the high and low-temperature cycle test is selected as follows:

The temperature cycle range is shown in Fig. 1-1:
The test was kept at 25 °C, 70 °C and -40 °C for 1 h to stabilize the temperature of the rubber test piece; to minimize the temperature load on the sample, the temperature conversion rate was selected to be 0.375 °C/min, 0.542 °C/min, both less than 1 °C/min, one cycle period T is 12h. The test selected 2 (1d), 6 (3d), 14 (7d), 30 (15d), 42 (21d), 60 (30d), 120 (60d) cycle times as sampling time, in order to avoid impact of peroxide of aged oil generated during the aging process, the test oil is periodically replaced.

3. Results and discussion

3.1. Results and analysis of mechanical performance test
The relationship between tensile elongation and tensile strength of nitrile rubbers under two different mediums is shown in Figure 2 and Figure 3:
It can be seen from Figure 2. and Figure 3. that the tensile elongation and tensile strength of the nitrile rubber decrease with the aging time. The elongation of the nitrile rubber sample stored in the oil medium after aging for 60 days is 265%. The tensile strength decreases rapidly in the early stage of aging, and decreases slowly in the middle and late stage of aging, which is different from the variation in the accelerated aging test in high temperature (the mechanical properties of the nitrile rubber in the thermal aging test are that the maximum tensile strength in the early stage of storage increased slightly and remained basically unchanged; the maximum tensile strength decreased rapidly in the later stage of storage). According to the analysis, the reason for this difference is mainly that in the rubber manufacturing process, to make the rubber have higher anti-swelling property, wear resistance and the like, rubber such as carbon black, lignin, calcium carbonate, etc. may be added to the rubber. the filler gradually dissolves and falls off under the action of the cyclic temperature load and the oil molecules in the medium, and the three-dimensional grid structure characteristics of the rubber elastomer are changed so that the mechanical properties of the rubber sample in the early stage of storage are rapidly decreased.

3.2. Results and analysis of compression set test

Nitrile rubber compression set - time curve is shown in Figure 4.

Analysis of Figure 4. shows that the rubber samples stored in the air medium gradually increased with the aging time in the early stage of the test and remained unchanged in the later stage of the test. The compression set rate of the aged rubber sample in the oil medium tends to increase first and then
remains unchanged with the increase of storage time. It can be concluded that under the action of pressure and temperature load, the rubber forms a new crosslink bond on the one hand, and on the other hand, the main chain breakage molecule loses flexibility, resulting in a tendency of the rubber compression set to gradually increase, while in the oil, the compression set rate of the rubber stored in the medium decreased in the later stage of the test. The intrusion of a small amount of oil medium under the cyclic temperature load caused pores and microcracks in the rubber matrix. As the time of accelerated aging increased, the microcracks continued to expand and the oil molecules further. Diffusion causes the rubber to swell and the compression set to recover.

3.3. Results and analysis of SEM

![SEM images of nitrile rubber](image1)

**Figure 5.** The sectional appearance of unaged nitrile rubber.

![SEM images of aged nitrile rubber](image2)

**Figure 6.** The sectional appearance of nitrile rubber aging in different days under cyclic temperature in air.
3.4. Results and analysis of Fourier infrared spectroscopy test

The molecular formula of the test nitrile rubber is shown in the figure below.

![Molecular formula of nitrile rubber](image)

**Figure 8.** The molecular formula of nitrile rubber.

![Infrared spectra of nitrile rubber aging in different days under cyclic temperature in air](image)

**Figure 9.** Infrared spectra of nitrile rubber aging in different days under cyclic temperature in air.
Figure 9 to 10 show the infrared spectra of different days of aging of nitriding rubber. The stretching peaks of the nitrile group (-CN) appear around 2221 cm$^{-1}$; the characteristic peaks at the wavenumbers of 2920 and 2849 cm$^{-1}$ are stretching vibration peak of methyl (-CH$_3$) and methylene (-CH$_2$)-; the in-plane deformation vibration absorption peak of the methylene group appeared around 1420 cm$^{-1}$; the bending vibration absorption peak of the double bond (C=C) in the butadiene chain link and the vinyl chain link appeared in the 960 cm$^{-1}$ and 911 cm$^{-1}$, respectively.

It can be seen from figure 9 that the characteristic peak absorption intensity of nitrile group, a methyl group and methylene group after 30 d aging of nitrile rubber stored in the air under temperature cycling conditions has little change, indicating that the nitrile group and single bond structure maintain at high-low temperatures condition. But the intensity of absorption peak of the C=C double bond in the butadiene and vinyl chain links is significantly decreased, indicating that the cyclic temperature and the oxygen, vapor in the air catalyze the double bond, which is consistent with the properties of high activity of double bond, weather resistance and UV aging resistance of nitrile rubber; No new characteristic peaks, red and blue shift of characteristic peaks in nitrile rubber appears throughout the aging cycle, in general, the basic structure of this type of rubber is relatively stable.

Under the conditions of high and low-temperature circulation, has a relatively long life under the air atmosphere. Compared with the infrared spectrum of unaged nitrile rubber, the nitrile rubber shown in figure 10 shows good oil resistance after aging for 30 days in the oil medium under the same temperature condition; the intensity of absorption peak of the nitrile group is almost no change, indicating that it has a good oil resistance in the early aging period due to the strong polarity of the group; the methyl. The intensity of absorption peak of the C=C double bond in the vinyl chain is only slightly reduced after 30 days, indicating that the molecular chain structure remains relatively intact during the aging medium, but the internal physical aging is more serious under the high-low cyclic temperature condition and the long-term corrosion in oil medium, which leads to a decline in its mechanical properties.

3.5. Results and analysis of dynamic mechanical properties test
Figure 11~12 show the curve of the storage modulus of the nitrile rubber under different temperature conditions.
The tangent value of the loss factor increases with the increase of aging time, and the temperature corresponding to the peak gradually moves toward the high-temperature direction, indicating that the glass transition temperature is gradually increased. It is considered that the cross-linking point disappears during the aging process of the nitrile rubber sample. The joint density is reduced, and there is a certain degree of main chain breakage and side group loss. In this process, the flexibility of the main chain is enhanced, and the molecular weight of the polymer decreases and the free volume increases, which causes the glass transition temperature of the sample to move toward the low temperature. Since the loss factor is the ratio of the energy dissipation modulus to the storage modulus, it can be confirmed that the loss modulus of the sample decreases faster during the aging process, that is, the molecular chain unwinding speed is greater than the rate at which molecules crosslink during the post-solidify and oxidation.

It can be seen from Figure 11 and 12 that the nitrile rubber has a higher modulus at -90 °C. With the increase of temperature, the storage modulus of the sample in the glass transition region is significantly reduced. When the temperature rises, the modulus of the elastic region hardly changes. The storage modulus of nitrile rubber stored in aviation kerosene decreased gradually from -90 °C to -20 °C with the increase of storage time, while the storage modulus of the transition zone and high elastic zone did not differ significantly with the increase of storage time.

The reason why the storage modulus of the nitrile rubber oil medium decreases with the aging time may be that, on the one hand, the rubber is entangled in the late stage of aging, the molecular weight decreases, and the modulus decreases; on the other hand, affected by the medium, the reinforcing agent and the filler gradually fall off, resulting in a decrease in the strength of the rubber.
Comparing the two graphs, the rubber energy consumption modulus shows a downward trend, indicating that the effect of swelling of rubber in the oil medium reduces the interaction between the rubber molecules and there is a large number of cross-linking point formed by the vulcanization is destroyed, so that the loss modulus of the rubber is greatly reduced under the pressure.

4. Conclusion
(1) Compared with the nitrile rubber sample stored in the air medium under temperature cycling conditions, the nitrile rubber material stored in the aviation kerosene medium decreases in tensile strength and elongation at break with the increase of the number of cycles, and the compression rate of permanent deformation increases, and the performance at the initial stage of aging decreases significantly.

(2) By analyzing the dynamic mechanical property curve and infrared spectrum, it can be seen that under the effect of cyclic temperature and oil, with the aging time prolonged, the nitrile rubber molecular chain flexibility is improved, the segment is untangled, and the cross-linking point Breakage, which is the main reason for the decrease in glass transition temperature and storage modulus of nitrile rubber.

(3) The fracture section of the rubber indicates that crack propagation due to the difference in thermal expansion coefficient between oil molecules and rubber matrix during aging and shedding of filler material caused by thermal stress are an important factor that causes the performance of nitrile rubber to decrease rapidly under cyclic loading.

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