



Influence of hydraulic oil on degradation behavior of nitrile rubber O-rings at elevated temperature

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ABSTRACT

The degradation of nitrile rubber O-rings exposed to hydraulic oil and air were investigated by adopting accelerated aging test. The chemical structures and mechanical properties of the aged samples were evaluated by measuring attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, crosslinking density, weight loss, mechanical properties and fracture morphology. The ATR-FTIR results indicate that chemical structure changed significantly due to loss of additives and oxidation reactions. Hydraulic oil and temperature played a critical role in surface chemical changes. The crosslinking density changes were attributed to the competition between crosslinking and chain scission. The mechanical test results show that there existed large differences in changes of mechanical properties for samples under different conditions, which correlated to loss of fillers, the changes in crosslinking density and the formation of defects. Additionally, the fracture morphologies demonstrate that the formation of hardened brittle outer layer, voids and agglomerates also promoted the decrease in mechanical properties.

1. Introduction

Nitrile rubber is well known for its good wear resistance, oil resistance and impermeability, and has been widely used as seals and gaskets in the sealing fields of oil and gas especially in hydraulic system such as piston seals, sealing of piston rods and axial sealing. However, due to the existence of unsaturated bonds and volatile components in rubber materials, the severe environmental factors such as oxygen, radiation, high temperature, aggressive media and mechanical stress can accelerate the aging process of seals, which leads to the degradation in mechanical properties and network structure [1–8]. Eventually, the seals lose the ability of deformation recovery, resulting in failure of sealing system due to leakages of gas and/or liquid [9,10]. Additionally, natural aging of rubber seals is a relatively slow process under actual working conditions, thus it needs a long time to gain the performance degradation data. Accordingly, the artificial accelerated degradation test conducted by simulating actual service conditions can be applied to investigate the degradation behaviors and mechanisms of rubber seals for shortening test duration.

When the seals are used in the hydraulic system of electro-hydraulic servo valve, they unavoidably are immersed into the hydraulic oil. During the immersion process, hydraulic oil gradually diffuses into the interior of seals, which led to swelling of rubber network structure. Furthermore, the coupled effect between hydraulic oil and temperature has a negative impact on thermal stability of rubber materials. Additionally, due to the complexity of rubber material compounds containing rubber matrix, various fillers and additives, the degradation of nitrile rubber materials immersed in hydraulic oil is an extremely complex process accompanied by a series of physical and/or chemical reactions [11,12]. The degradation of nitrile rubber materials in oil often occurs through the follow processes: the extraction of soluble components (e.g., plasticizers and antioxidants); the reactions of unsaturated bonds (e.g.,

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carbon-carbon double bonds and nitrile groups); thermal oxidative aging reactions (crosslinking and chain scission). Additionally, the loss of additives weakens the antioxidant ability of rubber matrix structure, and causes the worse compatibility between rubber matrix and additives [13]. The crosslinking and chain scission reactions make the network structure denser and denser, and restrict the movement of molecular chains [14]. Subsequently, these changes can affect seriously physical and mechanical properties of the seals. Besides, the oil type has a direct influence on oil resistance of the seals. The biodiesel has more excellent dissolving capacity than diesel fuel according to the principle of “like dissolves like” [13–15].

The degradation behaviors of nitrile rubber materials (mostly the unfilled rubber and rubber sheet) in oil have been studied extensively by many researchers. Pan et al. [11], and Akhlaghi et al. [16], reported the effects of crude oil and lubricant oil on the properties of hydrogenated nitrile rubber elastomer and radial lip seal. The deterioration of nitrile rubber [13,17], hydrogenated nitrile rubber [18] and the fuel hose [19] in different types of biodiesel such as palm biodiesel, rapeseed biodiesel and sweet oil were investigated. Buckley et al. [20], and Pazur et al. [21], showed the effect of liquid media on lifetime predictions of nitrile rubber O-rings. Additionally, the compatibility of nitrile rubber with diesel fuel [22], biodiesel [15,23] or their mixtures [13,24] were also studied. In spite of these significant efforts, most studies are limited to the performance degradation of nitrile rubber in oil. There are relatively less literatures focused on the degradation behaviors and mechanisms of the nitrile rubber O-rings in hydraulic oil.

The objective of this research is to investigate the degradation behaviors and mechanisms of nitrile rubber O-rings immersed in hydraulic oil at elevated temperatures (70 °C, 90 °C and 110 °C) by the systematic accelerated thermal aging tests. Meanwhile, the contrast tests of nitrile rubber O-rings exposed to air under the same conditions (temperature and aging time) were conducted to further reveal the influence of hydraulic oil on the degradation process. Subsequently, the changes in chemical structures of the aged samples were evaluated by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and solvent swelling test. The physical and mechanical properties of the samples before and after aging were assessed by weight loss, mechanical properties and fracture morphologies. By comparing and analyzing the changes in physical properties, mechanical properties and chemical structural of the samples under different aged conditions, we concluded how the hydraulic oil and elevated temperature affected the degradation behaviors and mechanisms of the nitrile rubber seals during the thermal aging process.

2. Experimental

2.1. Material and hydraulic oil

Vulcanized nitrile rubber O-rings with 35% acrylonitrile were provided by Changsha 5712 Aircraft Industry Corporation, Ltd, China. The material was compounded according to the formulation shown in Table 1, using a two-roll mill at a constant temperature of 151 °C and a pressure of 60 to 120 kg/cm² for 40 min. Then, the materials were processed into O-rings, which measured $\Phi 17 \text{ mm} \times 6 \text{ mm}$ (inner diameter \times cross section diameter, Fig. 1).

The hydraulic oil used in immersion test is 46# aviation hydraulic oil, which was supplied by Great Wall Lube Oil, China. Table 2 shows the main components of hydraulic oil for immersion test. The density of the hydraulic oil is 0.862 kg/L at 25 °C. The kinematic viscosity is 38.12 mm²/s at 50 °C. The flash temperature is 165 °C, and the acid value is 0.78 mg KOH/g.

2.2. Aging methods

To investigate the effect of hydraulic oil on the degradation behaviors and mechanisms of nitrile rubber O-rings, the accelerated aging tests (immersion in oil and exposure to air) were performed in air-circulating ovens. The immersion tests were conducted to simulate the hydraulic oil environment of O-rings in electro-hydraulic servo. The samples were placed in covered jars containing the hydraulic oil, which occupied 60% space of container. In addition, for comparison, the exposure tests in air were also conducted under the same aging conditions (temperature and aging time) with the immersion test. Then, the containers for immersion and exposure tests were placed in air-circulating ovens, and the test temperatures were selected at 70 °C, 90 °C and 110 °C. The aging time was 2 days, 4 days, 8 days, 16 days, 32 days and 64 days. To obtain the reliable results, each group of experiment set up three parallel samples for the following measurements.

Table 1
Constituents of the NBR samples.

Constituents	phr
Nitrile rubber	100
Zinc oxide	5
Sulfur	2.5
Carbon black	50
Plasticizer	18
Stearic acid	1.5
Antioxidant	2

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