

Investigation on thermal oxidative aging of nitrile rubber (NBR) O-rings under compression stress

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Abstract. The degradation behaviors of nitrile rubber O-rings exposure to air under compression were investigated at three elevated temperatures. The physical and mechanical properties of the aging samples before and after exposure at selected time were studied by measuring weight loss, tensile strength and elongation at break. The Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and fracture morphology were used to reveal the microstructural changes of the aging samples. The results indicate that the weight decreased with exposure time and temperature. Based on the results of the crosslinking density, the crosslinking predominates during the most of aging process. The significant changes in tensile strength and elongation at break also indicate the severe degradation in air. The fracture morphology results show that the fracture surface after 64 days of exposure to air turns rough and present defects. The ATR-FTIR results demonstrate that the hydroxyl groups were formed for the samples aged in air.

1. Introduction

NBR is widely used as seals for industrial and domestic applications due to its excellent performance including high resistance to oil, low abrasion rate and compressive stress resistance [1-3]. However, under actual service conditions, the O-rings are often subjected to harsh environment, such as mechanical stress (often the compressive stress), high temperature (up to 150°C), gas atmosphere and liquid environment, leading to the remarkably degradation for the seals [4-7]. Previous reports have focused on the degradation behaviors and mechanisms of nitrile butadiene rubbers in hot air under free state [8-12]. However, in the case of the actual service conditions, the seals are often designed to withstand the compressive stress to achieve the great sealing effect. The compressive stress can also result in the physical and chemical changes of the molecular structure and fillers, and has a direct influence on the degradation behaviors of seals [1]. Until now, just few reports have been available on the degradation of NBR O-rings under the compression state [13, 14]. For example, Zeng et al. [13] studied the corrosion mechanism of hydrogenated nitrile butadiene rubber O-ring under simulated wellbore conditions using self-designed compression simulator and autoclave. Kömmling et al. [14] investigated the effects of heterogeneous aging in compressed NBR and ethylene-propylene-diene rubber (EPDM) O-ring seals. Thus, the degradation behaviors of NBR O-rings exposure to air under compression still need to be further studied.

In this paper, we studied the long-term degradation behaviors of NBR O-rings exposure to air under compression at three aging temperatures by the accelerated testing. Then, the changes in chemical structures of the aged samples were investigated by ATR-FTIR. The physical and mechanical properties of the aged samples were also evaluated by measuring weight loss, mechanical properties and tensile fracture morphology. Then, on the basis of these results, we made an attempt to gain a better understanding of the degradation behaviors of NBR O-rings under the compression state.



2. Materials and methods

2.1. Material and Aging Methods

Nitrile rubber O-rings were supplied by Changsha 5712 Aircraft Industry Corporation, Ltd, China. The main components include NBR, zinc oxide, stearic acid, sulfur, carbon black and additives. An O-ring specimen at an inner diameter of 17.00 mm and a cross-sectional diameter of 2.65 mm. The accelerated aging tests were performed in the air-circulating ovens. In addition, the samples were oven-aged up to 64 days at 70°C, 90°C and 110°C.

2.2. Characterization Methods

Weight loss of the aged sample was measured by getting the average of the four parallel samples with electronic balance which has a resolution of 0.001 g. Mechanical properties of the aging samples were estimated by tensile tests. The tensile samples were tested according to GB/T 5720:1993 (China) using CMT5504 electronic testing machine at a strain rate of 50 mm/min. The tensile fracture morphology changes of the aging samples were analyzed by using scanning electron microscopy (SEM, JSM-6480). Attenuated total reflection-Fourier transform infrared (ATR-FTIR, Thermo Nicolet 6700) spectroscopy was applied to study the changes of chemical structure of the seals surfaces. The range of spectra is 400-4000 cm^{-1} with the resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Weight loss

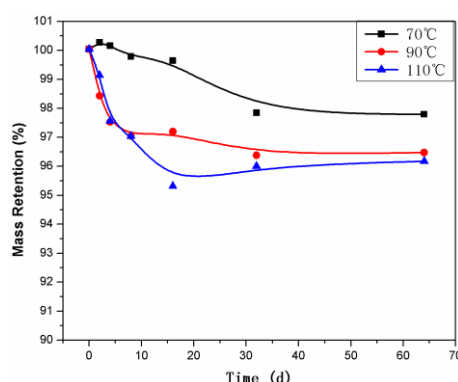


Fig 1. Weight loss of the compressed samples with the exposure time at different temperatures.

The changes in weight loss of the compressed samples at different temperatures are shown in fig 1. The weight loss increased with exposure time at 70°C. And the changes in weight show a similar trend at 90°C and 110°C. The weight loss increased remarkably during the first 4 days and then kept stable after 16 days of exposure. The higher the temperature, the more the weight loss. When the O-rings were exposed to air at high temperature, the volatile additives and residual monomers gradually migrated from the inner to surface by the action of elevated temperature, and then volatilized in atmosphere, resulting in the loss of the weight [10].

3.2. Mechanical properties

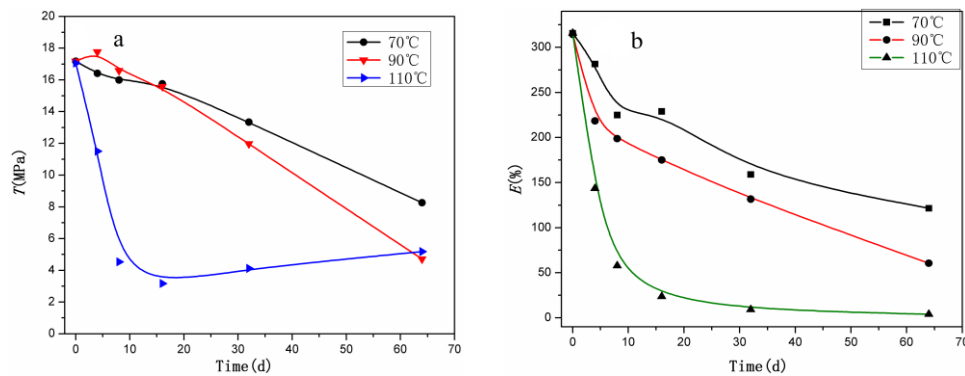


Fig 2. Changes in mechanical properties of the aging samples with the exposure time at different temperatures: a-tensile strength; b-elongation at break.

When the O-rings were subjected to the compressive stress, see fig 2, in the early stage, the stress caused the rearrangement of molecular chains accompanied by the decrease in free volume between the chains and the worse compatibility between the fillers and polymer matrix, which resulted in the slightly decrease of the tensile strength. However, in the early stage of aging at 90 °C, the appropriate crosslinking causes the increase in the tensile strength. For the compressed samples exposure to air, the consumptions of oxygen can meet the demand of the crosslinking reactions, resulting in the obvious increase of the crosslinking density and the formation of the denser network structure, which lead to the decrease in the tensile strength. But the limitation of oxygen diffusion, the stress and the elevated temperature cause the decrease in the crosslinking density and seriously destroy the matrix structure, leading to the decrease in the tensile strength. Meanwhile, the stress-induced and oxidation-induced physical and chemical degradations both result in the decrease in the elongation at break. These results demonstrate that the compressive stress and temperature have a great effect on the mechanical properties of the NBR O-rings.

3.3. Fracture morphology

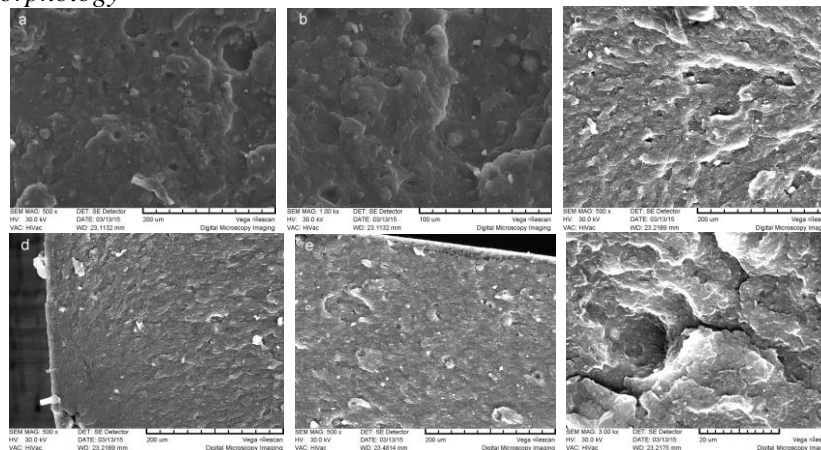


Fig 3. SEM of the tensile fracture surface of the aging samples at 110°C for different time.

The fracture morphology of the compressed samples before and after exposure to air at 110°C for different time is shown in fig 3. It is clearly seen that the obvious changes occurred in the fracture surface over time compared to the relatively smooth and uniform distribution of fillers fracture surface for the unaged samples. For the compressed samples after 64 days of exposure to air, the fracture surface (shown in fig 3 (c)) became rough and presented many secondary cracks, implying the characteristics of brittle fracture. Fig 3 (d) and fig 3 (e) show the formation of the hardened brittle outer layer. It is obvious that the hardened brittle outer layer contact with flanges is less pronounced than that exposure to air, implying the limitation of oxygen diffusion caused by flanges and the more serious degradation for the samples exposure to air. The fracture surface at a magnification of 3000X shows network crack

distributes desultorily in the polymer matrix, indicating the great changes for the network structure occurred.

3.4. ATR-FTIR analysis

To elevate whether the chemical degradation of the compressed samples exposure to air happened, the ATR-FTIR spectrum of the aged samples were investigated. Fig 4 shows the ATR-FTIR spectra of the compressed samples before and after exposure to air at 70°C and 110°C, respectively. The peak at 3394 cm^{-1} is assigned to the stretching vibration of the O-H band, implying the formation of the hydroxyl group. The peaks at 2918 cm^{-1} and 2843 cm^{-1} are attributed to the C-H stretching vibration of the CH_2 group. The peak at 2232 cm^{-1} is assigned to the $-\text{CN}$ stretching vibration. The peaks at 1733 cm^{-1} and 1533 cm^{-1} correspond to the C=O stretching vibration, indicating the presence of additives such as stearic acid and curing package. The peak at 1433 cm^{-1} is from the C-H bending vibration of the CH_2 group. The peak at 962 cm^{-1} is attributed to the C-H deformation vibration of the trans-1, 4-structure of the butadiene part.

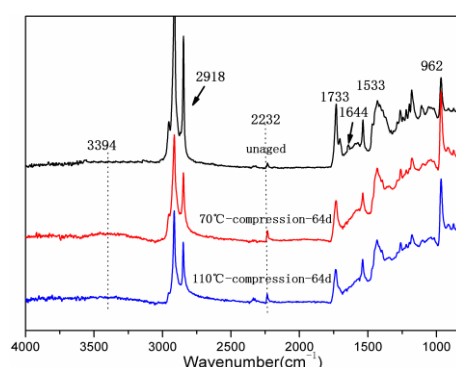


Fig 4. ATR-FTIR spectra of the aging samples with the exposure time at 70°C and 110°C.

By comparing the spectrum of the compressed samples after exposure to air at 70°C and 110°C, it can be clearly seen that the intensity of the peak at 3394 cm^{-1} increased obviously for the aged samples with aging time, which indicated that hydroxyl groups were generated due to the oxidation of the samples during the degradation process. For the samples after exposure to air, the peak at 1733 cm^{-1} first increased and then decreased with increase in aging time, implying the formation and consumption of carboxyl groups. It can be concluded that the carboxyl groups and hydroxyl groups were formed for the compressed samples exposure to air during the aging process.

4. Conclusions

The degradation of the NBR O-rings under the compression state exposure to air at elevated temperature were studied. It can be concluded that, during the aging process, the weight loss increased sharply first and then remained constant with exposure time and temperature, indicating the migration of fillers. The changes in tensile strength and elongation at break implying the serious degradation for the compressed samples exposure to air. The fracture morphology shows that the defects (voids and agglomerates) and the hardened brittle outer layer were generated in the fracture surface. The ATR-FTIR results indicate that hydroxyl groups and carboxyl groups were formed for the samples aged in air.

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