Durability of O-ring rubber seals to hot water containing residual chlorine for appliances

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1. Abstract

O-ring rubber seals are widely used for hot water pipes of various kinds of residential gas appliances. Their degradation such as cracking and carbon black bleed-out is caused by heat damage and chemical reaction due to the residual chlorine in water, and it has been one of the most important concerns. There are many kinds of O-ring rubber seals in terms of the polymer material, the filler and the crosslinking types, and the way of the degradation differs depending on them. Therefore their effect on the degradation of O-ring rubber seals investigated in this study.

The tests were conducted using eight kinds of commercial O-rings with the same size. The six of them were made of ethylene propylene diene rubber, EPDM, and the rest were made of fluorocarbon rubber, FKM. The compression set, the weight and the compressive load-displacement were measured after the accelerated aging in hot water with and without chlorine.

The result of the compression set measurements showed that the obvious degradation was not observed until 10,000 hours for all of the eight O-rings, and that the chlorine effect was not observed either. On the other hand, it was shown that the weight and the compressive load of the three EPDM O-rings with the carbon black were decreased under the chlorine water aged condition. This is thought to be caused by the carbon black bleed-out and the oxidation due to the chlorine existence. In addition, the weight and the compressive load of the FKM O-rings with the polyol-crosslinked structure and the carbon black were decreased not depending on the chlorine existence. This is thought to be caused by the moisture absorption of the acid acceptor.

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2. Introduction

O-ring rubber seals are widely used for hot water pipes and various kinds of residential gas appliances for hot water supply. The durability and stability of these pipes and appliances play a critical role in customer satisfaction with gas utility companies because the supply of hot water constitutes a major use of city gas for residential customers.

O-rings are key components in pipes and appliances, because their degradation affects the durability and stability. When O-rings are used in hot water systems, degradation is induced by residual chlorine in water [1], which is used as a disinfectant to prevent the spread of infectious diseases [2-3]. Residual chlorine is known to cause molecular chain scission/re-bonding in rubber materials, which leads to the contamination of water by fragments of degraded rubber [1]. Furthermore, the degradation of O-ring rubber seals can be accelerated at elevated temperatures in hot water appliances.

The durability of rubber exposed to hot water containing residual chlorine has been investigated in several studies. The degradation of ethylene propylene diene rubber, EPDM, filled with carbon black has been studied by several researchers [1, 4-8]. Furthermore, Mitsuhashi et al. reported that the molecular weight of acrylonitrile butadiene rubber in diaphragms decreased after several years of exposure to tap water containing residual chlorine [9]. Nakamura et al. compared the degradation behavior of several compounds with different base polymers and fillers such as carbon black and silica upon exposure to water containing chlorine for 72 h [10-11]. Though there are several studies on the durability of rubber exposed to hot water, differences in the degradation behavior of different types of rubber over time under the same conditions has not been compared or discussed.

In this study, we exposed several kinds of commercial O-rings having same size and different compounds to hot water with and without chlorine for up to 18,000 h. We investigated, compared, and discussed the degradation behavior of various types of rubber compounds under different exposure conditions. Optical microscope observations and measurements of compression set, CS, and weight change ratio of aged O-ring samples were carried out. Additionally, the compressive load against displacement, namely the repulsive force against the compressive deformation, of the O-ring samples was examined. Though the compressive load against displacement is expected to bemore directly related with seal ability than CS, it is not generally used as a parameter to evaluate degradation of rubber seals. We investigated the applicability of compressive load against displacement as a parameter for evaluation of degradation of O-rings aged in hot water with and without residual chlorine.

3. Experiment

3.1. Materials

Eight commercial O-rings of the same size and different compounds were tested. The inner diameter of the O-rings was 15.8 mm and the wire diameter was 2.4 mm. Either EPDM or fluorocarbon rubber, FKM, was used as the base polymer for each O-ring. The base polymer and major reinforcement filler of each O-ring is described in Table 1. The base polymers of the O-rings were examined by Fourier transform infrared spectroscopy (FT-IR) analysis, pyrolysis gas chromatography mass spectrometry (Py/GC-MS), and nuclear magnetic resonance (NMR). The major reinforcement fillers were investigated by thermogravimetric (TG) analysis, X-ray diffraction (XRD), FT-IR, and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Table 1. Base polymer and major reinforcement filler of O-ring samples.

O-ring sample	Base polymer	Major reinforcement filler
EPDM1	EPDM	Carbon black
EPDM2	EPDM	Carbon black
EPDM3	EPDM	Carbon black
EPDM4	EPDM	Silica
EPDM5	EPDM	Silica
EPDM6	EPDM	Silica
FKM1	FKM	Aluminum oxide
FKM2	FKM	Carbon black

3.2. Immersion aging test

All O-ring samples were compressed and set between two steel plates and fastened with bolts and nuts, as shown in Fig. 1. They were compressed by 25% with 1.8 mm-thick spacers. All O-ring samples were then immersed in hot water with and without chlorine at 70°C in thermostatic containers for 250 to 18,000 h. The concentration of chlorine in the containers was controlled to be 5 ppm.

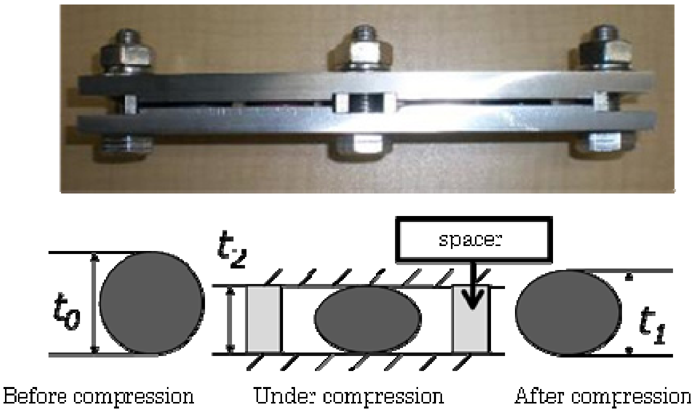

Figure 1. Schematic illustrating O-ring samples compressed between two steel plates and fastened by bolts and nuts and the thickness under each condition.

3.3. Analysis

3.3.1. Optical microscope observations

Optical microscope observations were conducted to examine the surface degradation of O-ring samples aged in hot water with and without chlorine.

3.3.2. Compression set (CS)

CS is expected to be related to seal ability and is generally considered a useful parameter in the evaluation of rubber seal degradation. CS is described by the following equation:

$$CS[\%] = \frac{t_0 - t_1}{t_0 - t_2} \times 100 \quad \cdots(1)$$

where t_0 is the thickness of the original specimen of each O-ring sample, and t_1 is the specimen thickness after immersion. t_2 is the thickness of the spacer (1.8 mm). The thickness of t_0 and t_1 were measured before and after immersion.

3.3.3. Weight change ratio

The weight change ratio (WCR) of each specimen was determined by equation 2

$$WCR[\%] = \frac{m_1 - m_0}{m_0} \times 100 \quad \cdots(2)$$

where m_0 and m_1 are the weight of each O-ring sample before and after immersion.

3.3.4. Compressive load displacement

A compressive load was applied on the upper surface of each O-ring in a load-testing machine (MAX-1KN-H) with a 1000 N load cell. The compressive load against the load cell displacement was measured as the repulsive force of the O-ring samples at 1 μm intervals, between 2.6 and 1.6 mm as a distance from the bottom plate of the testing machine on which the O-ring sample was placed.

4. Results and discussion

Microscope observations revealed that there were no cracks or voids on the surfaces of the O-ring samples aged in hot water without chlorine. Conversely, numerous cracks and voids were observed on the surface of EPDM2 aged in hot water with 5 ppm chlorine for 18,000 h, as shown in Fig 2(a). Numerous cracks and voids were also observed on the surface of EPDM1 and EPDM3 aged under the same conditions as EPDM2. Several authors have reported the fragmentation of degraded EPDM with carbon black owing to the presence of chlorine in water [1, 4-6]. The voids on the surface of EPDM1-3, which has carbon black as a reinforcement filler, indicated that degraded EPDM fragments broke away from the surface of the O-rings. Microscope observations revealed that the surface of EPDM 4-6, aged in hot water with 5 ppm chlorine, was covered with a white substance. Figure 2(b) depicts the formation of substances on EPDM4 aged in hot water with 5 ppm chlorine for 18,000 h. The white substances have not been identified yet. On the other hand, no cracks, voids, or substances were observed on the surfaces of FKM1 and FKM2 under the same conditions. Figure 2(c) shows the surface of FKM1 aged in hot water with 5 ppm chlorine for 18,000 h.

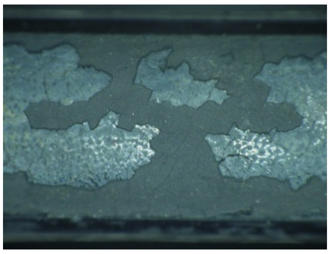

Figure 2(a). Cracks and voids observed by microscopy for EPDM2 aged in water with 5 ppm chlorine for 18,000 h.

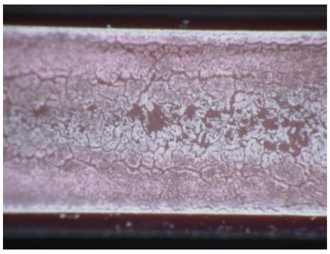

Figure 2(b). White substances on EPDM4 aged in hot water with 5 ppm chlorine for 18,000 h.

Figure 2(c). No cracks, voids, or substances were observed on the surface of FKM1 aged in water with 5 ppm chlorine for 18,000 h.

Figure 3(a) shows the CS of the O-ring samples against aging period in hot water without chlorine. The values of CS at 18,000 h varied between 12 and 37%, depending on the composition of the rubber. The CS of the O-ring samples aged in hot water with 5 ppm chlorine is plotted against aging period in Fig. 3(b). The values of CS at 18,000 h were between 10 and 36%. There was no significant difference in the CS owing to the presence of chlorine. Skidmore reported that a CS of 80 or 90% is a valid failure criterion for rubber seals [12]. The highest CS value of 37%, even at 18,000 h, was much lower than 80%. Therefore, the CS measurements did not indicate obvious degradation of O-ring samples aged in hot water with or without chlorine.

The WCR of the O-ring samples is plotted against aging period in hot water without chlorine in Fig. 4(a). The weight of all the samples, with the exception of FKM2, did not change with aging time in hot water without chlorine. The WCR of FKM2 changed by 13% after 18,000 h. XRD analysis of FKM2 indicated that FKM2 contained calcium hydroxide, an acid acceptor. Since calcium hydroxide can easily absorb moisture, the increase in weight for FKM2 may have been caused by moisture absorption owing to the presence of calcium hydroxide. Figure 4(b) depicts a plot of WCR against aging period in the presence of 5 ppm chlorine. The WCR of FKM2 was 12% at 18,000 h in hot water with 5 ppm chlorine. There was no significant difference of the WCR of FK2 between with and without chlorine. The weight of each sample of EPDM with carbon black, namely EPDM1-3, decreased upon aging in hot water with chlorine. For instance, the WCR of EPDM1 was -18% at 18,000 h. The decrease in the weight of EPDM1-3 was caused by the degradation and breaking away of EPDM fragments from the surface of the sample, as described above. The weights of two kinds of EPDM with silica, EPDM4 and EPDM6, also decreased upon aging. For example, the weight of EPDM4 decreased by 8.7% at 18,000 h. However, the reason for the decrease in the weight of EPDM4 and EDPM6 could not be determined in the present study. Interestingly, the weight of EPDM 5 and FKM1 did not change upon aging.

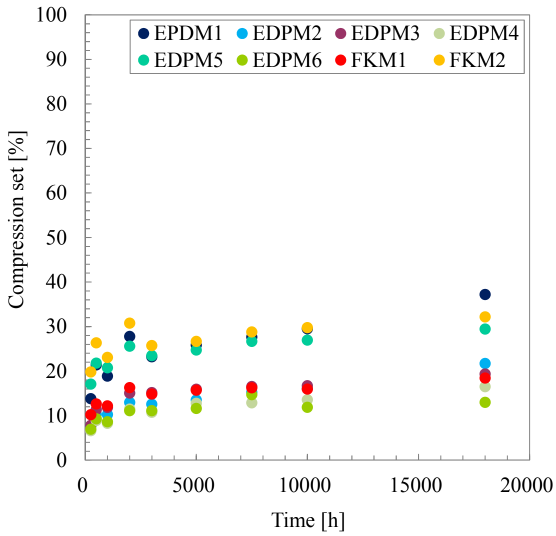

Figure 3(a). Plots of compression set against aging period in hot water without chlorine.

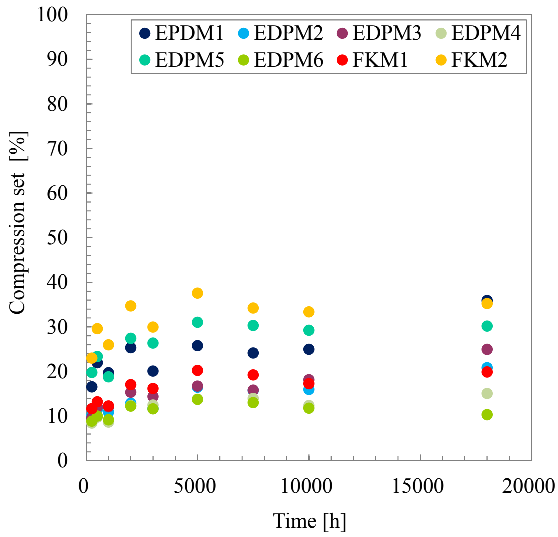

Figure 3(b). Plots of compression set against aging period in hot water with 5 ppm chlorine.

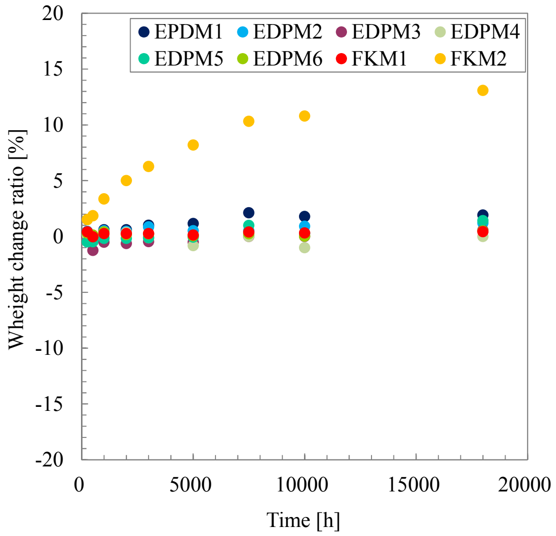

Figure 4(a). Plots of weight change ratio against aging period in hot water without chlorine.

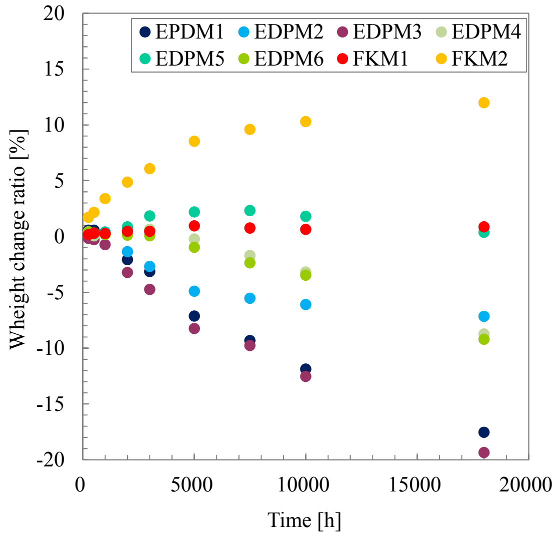

Figure 4(b). Plots of weight change ratio against aging period in hot water with 5 ppm chlorine.

Though the measurements of WCR and optical microscope observations implied that residual chlorine can accelerate the degradation of EPDM with carbon black in hot water, no obvious differences in CS were observed owing to the presence of chlorine. Therefore, we examined the compressive load against the displacement of the upper surface of the O-ring samples aged for 7,500 h and longer, because compressive load against displacement, namely repulsive force, is expected to be strongly related to seal ability. Since the O-ring samples were compressed by 25 % in the immersion test, we compared the difference in compressive load of each sample at a compression ratio of 25%.The compressive load of each O-ring sample was normalized by dividing that of each non-aged O-ring sample, because there was significant difference in the compressive load values of non-aged O-ring samples.

Figure 5(a) shows the normalized compressive load of EPDM1-3 versus aging period. With the exception of EPDM3 aged in hot water without chlorine, the normalized compressive load decreased with aging time. The normalized compressive load values of EPDM1 at 18,000 h aged in hot water with and without chlorine were 0.75 and 0.83, respectively. In the case of EPDM1-3, namely EPDM with carbon black, the normalized compressive load decreased more rapidly in hot water with 5 ppm chlorine than that without chlorine. The normalized compressive load of EPDM4-6 is plotted against aging period in Fig. 5(b). Though the normalized compressive load of EPDM4 aged in hot water with 5 ppm chlorine was lower than that without chlorine at 7,500 and 10,000 h, the former was higher than the latter at 18,000 h. The

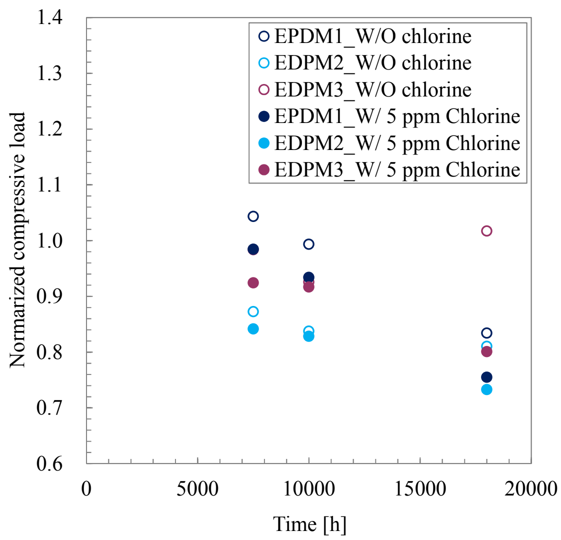

Figure 5(a). The normalized compressive load at a compression ratio of 25% for EPDM1-3.

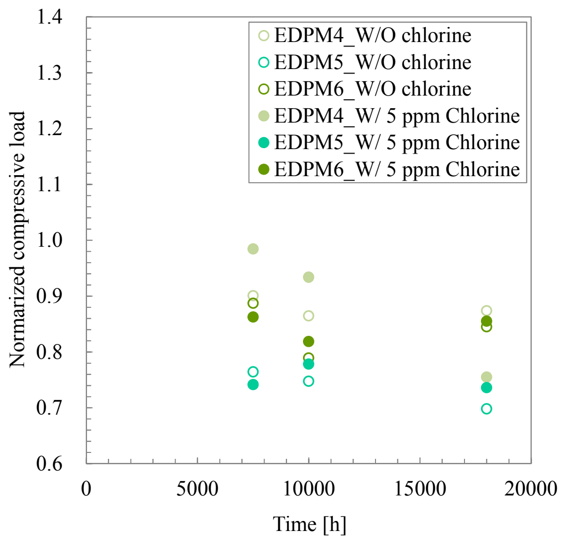

Figure 5(b). The normalized compressive load at a compression ratio of 25% for EPDM4-6.

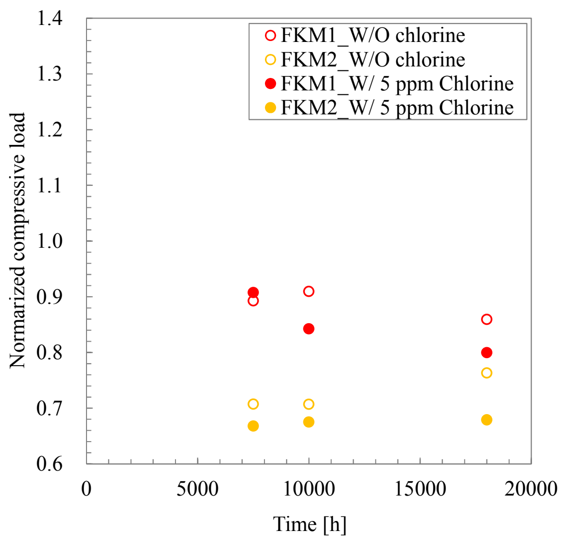

Figure 5(c).The normalized compressive load at a compression ratio of 25% for FKM1-2.

residual chlorine in hot water did not obviously affect the compressive load of EPDM4-6, namely EPDM with silica. Figure 5(c) presents the normalized compressive load of FKM1-2 aged in hot water with and without chlorine versus aging period. Though the compressive load of aged FKM O-ring samples was lower than that of the non-aged samples, it did not obviously decrease with aging time with the exception of FKM1 aged in the presence of 5 ppm chlorine. The normalized compressive load of FKM1-2 aged in hot water with 5 ppm chlorine was nearly equal to or lower than that without chlorine for each aging period.

The compressive load against displacement measurements revealed that the seal ability of EPDM O-ring samples with carbon black degraded faster in hot water with residual chlorine than without chlorine. Additionally, the compressive load against displacement measurements, namely the repulsive force of O-ring samples, is obviously more applicable and practical than CS in the evaluation of the degradation of O-ring rubber seals.

5. Conclusions

To evaluate the durability of O-rings exposed to hot water, we immersed several kinds of commercial O-rings that have same size and different compounds in hot water with and without chlorine and then compared the difference in degradation behavior. The measurements of WCR, optical microscope observations, and compressive load against displacement measurements revealed that the seal ability of EPDM O-rings with carbon black can degrade faster in hot water with residual chlorine than without chlorine. Additionally, the results of this study indicate that compressive load against displacement is more applicable and practical than CS in the evaluation of the degradation of O-ring rubber seals.

6. Acknowledgement

This work was performed in the collaboration among Kyoto Institute of Technology, Osaka Gas Co., Ltd, Toho Gas Co., Ltd, and Tokyo Gas Co., Ltd. The authors would like to acknowledge Prof. Nishimura, Prof. Hotta, Mr. Y. Tani, and Mr. Y. Yokohama of Kyoto Institute of Technology.

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