Degradation Mechanism of EPDM Packing with Chlorine in City Water

Ethylene-propylene-diene rubber · Carbon black · Degradation mechanism · Chlorine water · EPMA · XPS · NMR

Degradation of crosslinked ethylene-propylene-diene rubber (EPDM) with chlorine-containing compounds was investigated in water, in order to elucidate a mechanism of the degradation of EPDM seal used for a city-water-supplying system. Two crosslinked EPDMs were prepared by crosslinking with sulfur, ZnO, accelerator and so forth after mixing with two kinds of carbon black (ie.HAF and FT), respectively. They were degraded in chlorine water. Change in morphology of the rubbers due to the degradation was observed by scanning electron microscopy. The effect of water on the degradation was examined by EPMA. X-ray photoelectron spectroscopy (XPS) revealed that the crosslinked EPDM mixed with HAF was easier to absorb chlorine and to be degraded than the one mixed with FT, since Cl(2p) peak was detected from the crosslinked EPDM after degradation. It was found that the degraded EPDM was brittle, collapsed and fell off, based on the fact that the chlorinated methyl group of the crosslinked EPDM reacted with the other molecular chains of the EPDM, as is evident from an increase in crosslink density.

Abbau-Mechanismen von EPDM Verpackungen mit chlorhaltigem Wasser

Ethylen-Propylen Kautschuk · Ruß · Abbaumechanismus · chlorhaltiges Wasser · EPMA · XPS · NMR

Der Abbau von vernetzten EPDM-Proben durch chlorhaltiges Wasser wurde untersucht um den Mechanismus des Abbaus von EPDM-Dichtungen im Wasserversorgungssystem aufzuklären. Zwei mit unterschiedlichen Rußen (HAF und FT) gefüllten und mit Schwefel/Beschleuniger vernetzten EPDM Proben wurden in chlorhaltigem Wasser abgebaut. Die eintretenden Änderungen der Morphologie wurden mit Rasterelektronenmikroskopie verfolgt. Mit Hilfe von EPMA wurde der Effekt von Wasser untersucht. Durch XPS wurde gezeigt, dass mit HAF gefüllter EPDM mehr Chlor absorbiert und leichter abgebaut wird als der mit FT gefüllte Kautschuk. Die Versprödung des EPDM wird auf die Reaktion der chlorieten Methylgruppen mit benachbarten Ketten und die damit verbundene Vernetzung zurückgeführt.

Figures and Tables:
By a kind approval of the authors

Ethylene-propylene-diene rubber (EPDM) is commonly used in severe environments because it is a versatile elastomer with excellent resistance to water, chemicals, and ozone. These features make EPDM the elastomer of choice for rubber used in conjunction with water supplies in urban areas. However, recent environmental pollution has accelerated the deterioration of the water quality in metropolitan areas. The residual chlorine concentration in city water has increased due to countermeasures against water quality deterioration, and consequently, the number of reported cases of EPDM rubber degradation due to residual chlorine has increased in the last 15 years. In addition, recent improvements in the standard of living have prompted people to use warm water in their everyday lives, which has had a compounding effect. Namely, the residual chlorine and high temperature are causing EPDM rubber surfaces used in the water supply to disintegrate in a short period of time. Despite these facts, few systematic analyses have examined the degradation mechanism of EPDM rubber due to residual chlorine [1-4].

Previously we conducted a survey on the breakage incident of EPDM rubber packing to determine if residual chlorine is the main cause of detoriation. Instead of water leak, a number of black objects, which measured 1 mm by 1 mm or smaller, came out of a faucet installed 10 months prior. Our analyses using Fourier Transform Infrared Spectroscopy (FT-IR) and Pyrolysis Gas Chromatography (PGC) revealed the black objects were EPDM rubber. This result led us to compare the composition and physical properties of new packing and deteriorated packing after 10 months of use (Tables 1 and 2). Table 1 shows that the new and used packing have the same composition, indicating exposure to city water or a breakdown due to physical and mechanical factors does not extract components of EPDM rubber. However, Table 2, which depicts the physical properties, demonstrates typical degradation of EPDM rubber where hardness and tensile strength increase despite identical compositions.

Hence, a further study was conducted to analyze the substances causing degradation using an Electron Probe Microanalyzer (EPMA) for an assay and cross-sectional line analyses. This study revealed that unlike new packing, the used packing has a large amount of chlorine on the surface (down to a depth of ~140 μm) (Fig. 1). Additionally, oxygen was present, suggesting that oxidation occurs simultaneously with adsorption and diffusion of chlorine. The analyses revealed the degradation process of EPDM rubber packing involves multiple factors: chlorination by chlorine and oxygen in the water, crosslinking associated with oxidation, and embrittlement due to simultaneous decomposition. This led to stress cracking and water flow, which caused physical flaking and mechanical breakdown of the packing. However, a detailed degradation mechanism is unknown and systematic analysis has yet to be conducted.

In this work, we present novel knowledge obtained by systematic structural analyses to clarify the damage mechanism that a minute amount of residual chlorine in city water has on EPDM rubber. Various analytical methods were used to examine EPDM rubber samples, which were degraded by immersing in chlorinated water.

Experiment

Samples

We hypothesized the residual chlorine degrades carbon black (CB), which causes EDPM rubber degradation because CB not

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bonded to an EPDM molecule is highly attractive to chlorine and the amount of CB formulated in EPDM rubber is second to that of polymer. Hence, we prepared two types of vulcanized EPDM rubber samples. Their chemical structures and physical properties were compared after immersing them in chlorinated water. Sample 1 was high abrasion furnace (HAF) black, which had a relatively small diameter (i.e. a large specific surface area). Sample 1 served as a representative furnace black with a large functional group distribution containing oxygen on the surface. Sample 2 had a relatively large diameter (i.e. a small specific surface area), and fine thermal (FT) black was chosen as a representative thermal black with a small distribution of functional groups containing oxygen on the surface. Table 3 shows the formulations of two types of EPDM rubber. Commercially available EP3 (made by JSR Corporation, ethylidene norbornene (ENB), content 8.1 wt%, as the diene) was used as an EPDM polymer and commercially available vulcanization promoters, tetramethylthiuram disulfide (TMTD) and 2-mercaptobenzothiazole (MTB), were employed. HAF black (sample 1, particle diameter 26 to 30 nm) and FT black (sample 2, particle diameter 101 to 200 nm) were used as CB. Table 3 describes the other formulation and vulcanizing conditions, which were based on standard formulations. The components were roll-kneaded, and then formed into 2-mm thick vulcanized sheets.

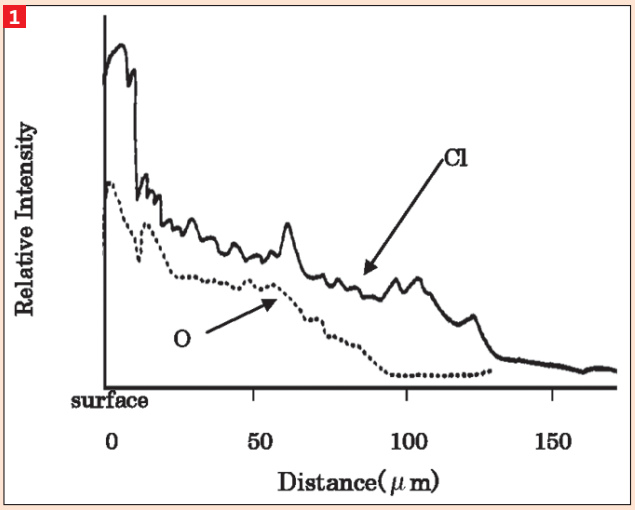
Degradation process

500-ppm chlorinated water (Kanto Chemical Co., Inc.) was formulated by adding ion-exchanged water. Immersion in this water for 2 hours at 40 °C degraded the samples, which were then dried under reduced pressure for 24 hours at room temperature and used in the various analyses. To promote rapid degradation, this chlorinated water had a much higher chlorine concentration compared to city water.

Analyses and measurements

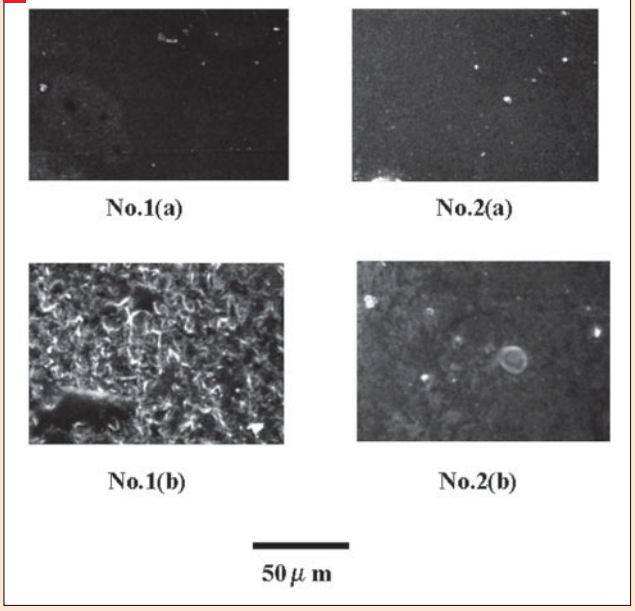
The sample surfaces were observed using a scanning electron microscope (SEM) from JEOL, JSM-T300 at an acceleration voltage of 10 kV and 500× magnification. The water content in each sample was measured using a coulometric moisture titrator, CA-06, and water vaporizer, VA-06, which were both from Mitsubishi Chemical Karl Fischer, at a heating temperature of 150 °C. Electron probe microanalysis (EPMA) was performed using EPMA-1600 from Shimadzu at an acceleration voltage of 15 kV and beam current of 0.06 uA. The network chain concentration was obtained using the Flory-Rehner equation in swelling method with benzene as swelling solution. Additionally, X-ray photoelectron spectroscopy (XPS) was performed using JPS-9010MC from JEOL at X-ray output power of 100 W.

1



1 Chlorine (–) and oxygen (···) profiles of EPMA spectra in the cross section of EPDM packing used for 10 months in city water.

2



2 Surfaces of EPDM rubbers (a) before and (b) after corrosion treatment (by SEM observation): No. 1, HAF black stock and No. 2,FT black stock.

1 Composition analyses of the EPDM packings

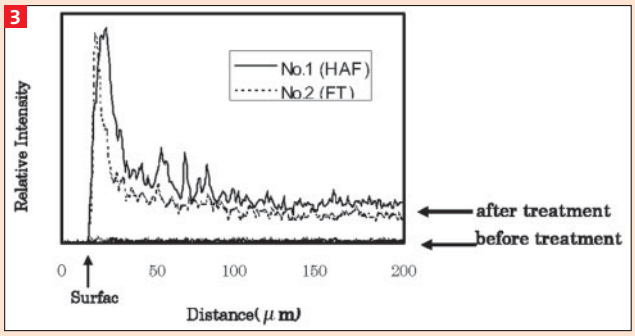
	before use	after use (10 months)
Qualitative analysis	EPDM	EPDM
Acetone extraction content(%)	24.1	24.3
Rubber content(%)	40.2	40.5
CB content(%)	30.1	30.4
Ash content(%)	4.3	4.4

2 Physical properties of the EPDM packings

	before use	after use (10 months)
Hardness (IRHD)	55	60
Tensile strength (MPa)	10.8	12.0
Elongation (%)	700	390

3 Formulations of the rubber samples

materials	Compounds No.1	Compounds No.2
EPDM	100	100
Zinc oxide	5	5
Stearic acid	1	1
Naphthenic oil	50	50
CB(HAF)	80	–
CB(FT)	–	80
Sulfur	1.5	1.5
Accel. TMTD	1	1
Accel.MBT	0.5	0.5
Cure conditions	160 °C× 15 min.	160 °C× 10 min.



3 Depth profiles of relative chlorine intensity on the cross section of EPDM rubbers before and after corrosion treatment: No. 1,HAF black stock (–) and No. 2, FT black stock (···).

4 Increase in water amount by the corrosion treatment

Sample	Increase in water amount (%)
No. 1 (HAF)	+0.49
No. 2 (FT)	+0.28

Results and Discussion

Surface condition observations using SEM

Figure **2** shows the SEM images of sample surfaces before and after the degradation treatment using chlorinated water. Sample 1 (HAF) has a rougher surface with a greater unevenness compared to sample 2 (FT). The only compositional difference between samples 1 and 2 is the type of CB, suggesting CB greatly contributes to surface degradation.

Water quantity measurements before and after immersion using the Karl Fischer method

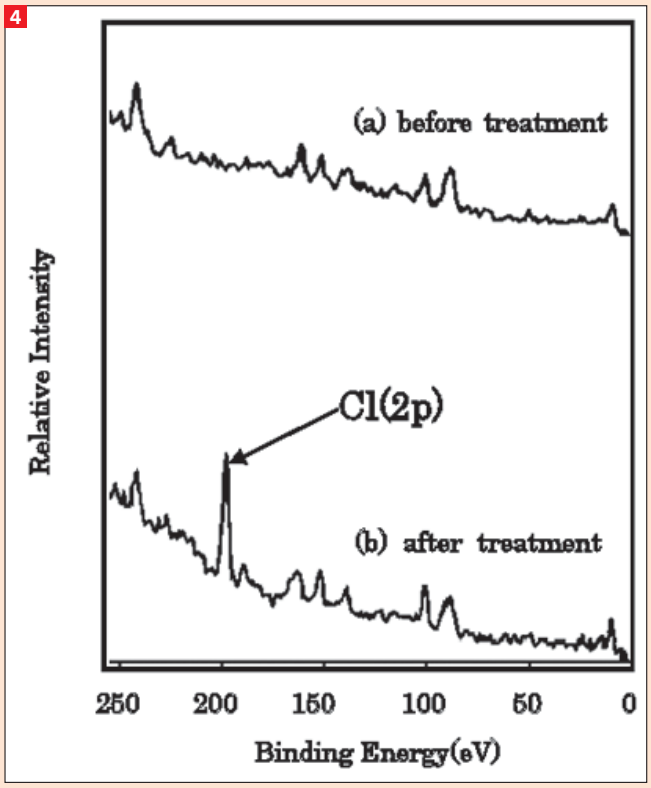
Because the surface after the degradation treatment is rougher for sample 1 (HAF) than sample 2 (FT), the Karl Fischer method was used to measure the water content. Table **4** shows the increased water content after degradation. The increase in the water content of sample 1 (HAF) is +0.49 %, which is almost twice that of sample 2 (FT, +0.28 %). This supports a stronger water adsorption for sample 1 because sample 1 has more specific surface of the CB content as well as a greater polarization due to more functional groups containing oxygen on the surface compared to sample 2.

Penetration measurements using EPMA

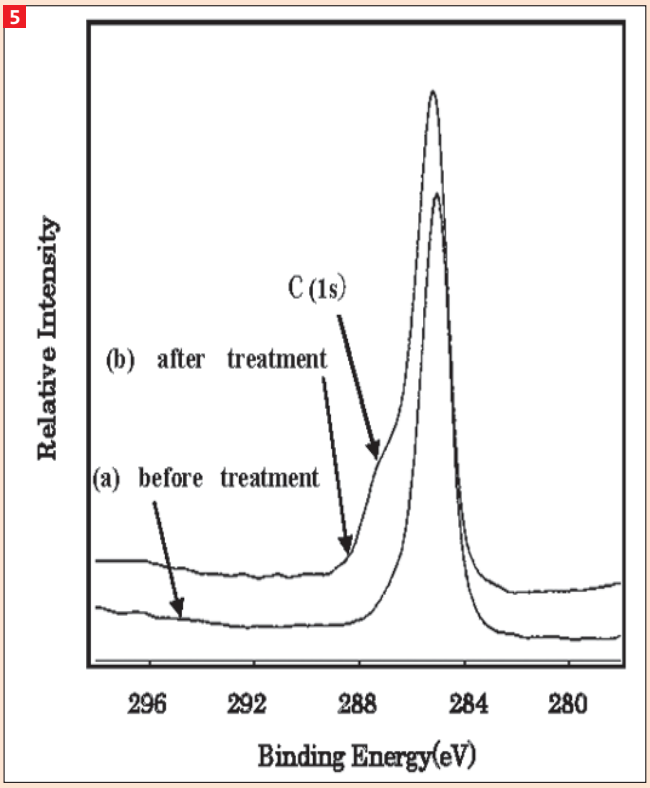
The large difference in water content between sample 1 (HAF) and sample 2 (FT) suggests the water penetration rate influences chlorine penetration. Hence, an EPMA line analysis was performed on cross-sections of EPDM rubber after immersion to observe the chlorine concentration from the surface to the core (Fig. **3**). The chlorine concentration exponentially decreases from the surface to the core for sample 1 (HAF), and reaches a constant value beyond a depth of 140 μm, confirming the chlorine compound is adsorbed by CB as the water is adsorbed. Additionally, the chlorine compound diffusion progresses at a much higher rate in sample 1 (HAF) than in sample 2 (FT).

Measurements of crosslinking density

It is possible that sample 1 (HAF) adsorbs chlorine compounds more strongly than sample 2 (FT), resulting in polymer damage. To evaluate the degradation of the polymer, a swelling method was employed to measure the change in crosslinking density. Table **5** shows the results. Although the degradation treatment has a negligible effect on sample 2 (FT), sample 1 (HAF) exhibits ~ 1.2-



4 XPS survey spectra of HAF black-loaded EPDM rubbers (sample No. 1) (a) before and (b) after corrosion.



5 XPS high resolution C (1 s) spectra of HAF black-loaded EPDM rubbers (sample No. 1): (a) before and (b) after corrosion.

5 Change of the crosslinking density by the corrosion treatment

Sample	crosslinking density (10^{-4}mol/dm^3)	
	Before treatment	After treatment
No. 1 (HAF)	2.69	3.36
No. 2 (FT)	1.46	1.49

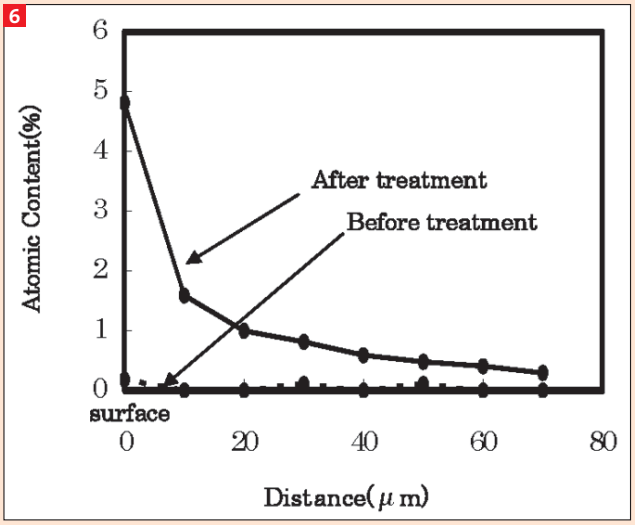
fold increase in the crosslinking density after the treatment. Thus, the network chain density increases on sample 1 (HAF), and consequently stiffening degradation occurs.

Evaluation of degradation mechanism using XPS

Because the chlorine treatment increases the network chain density in sample 1 (HAF), causing stiffening degradation, we investigated the degradation mechanism. Figure **4** shows the XPS spectra before and after chlorine treatment. After the degradation treatment, a Cl (2p) peak appears and the C (1s) peak includes a slight shoulder near 287 eV, suggesting the existence of a C-Cl bond (Fig. **5**). The results show that degradation generates C-Cl bonds. We further studied the depth profile of the Cl (2p) peak. C-Cl bonds are generated down to a depth of 60 to 70 μm (Fig. **6**), supporting the EPMA result shown in Figure 3. The XPS analysis revealed that C-Cl bonds are generated due to the degradation treatment.

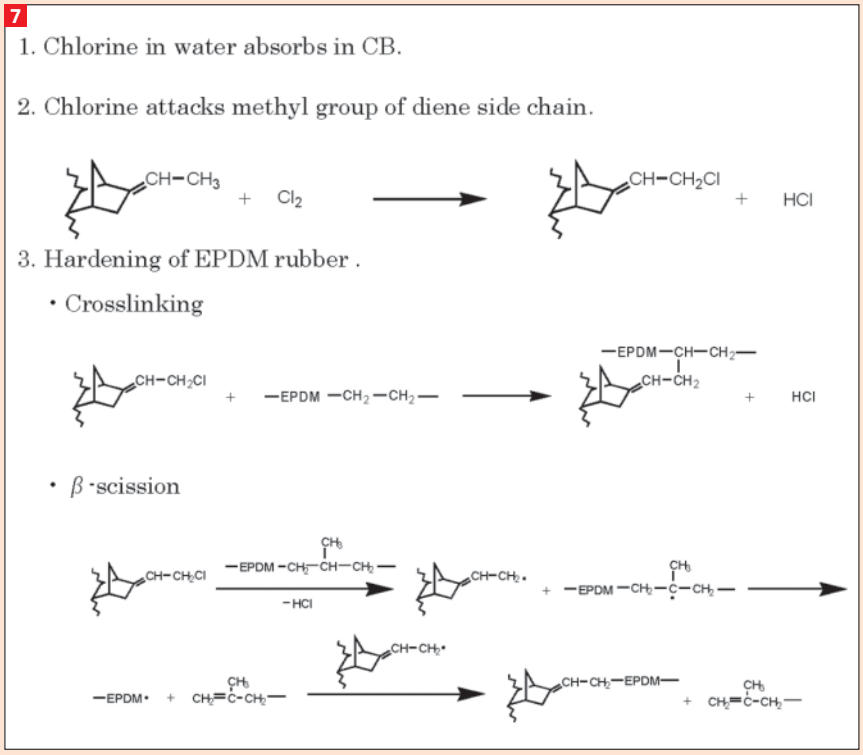
Figure **7** depicts the EPDM rubber degradation mechanism due to chlorinated water, which is inferred based on the above results. First, CB, which is part of EPDM rubber, absorbs chlorine in city water. Next, chlorine attacks the diene side chain of EPDM rubber and chlorinates the methyl groups. Third, the chlorinated methyl groups react with other EPDM rubber molecules to increase the crosslinking density. Consequently, the packing stiffens, leading to stress cracking and disintegration.

6



6 Depth profiles of chlorine atomic content on the cross section of EPDM rubbers (sample No. 1) before (···) and after (–) corrosion treatment.

7



7 Schematic degradation mechanism of EPDM rubber by chlorine water.

Summary

The differences in particle diameters and surface conditions of CB in EPDM rubber alter the adsorbability of chlorine in chlorinated water. EPDM rubber with HAF black and particle diameters between 26 and 30 nm adsorbs chlorine more readily than EPDM rubber with FT black and particle diameters between 101 and 200 nm. Hence, EPDM rubber with HAF black degrades more easily. However, the inferior initial physical properties of vulcanized EPDM rubber using FT must be carefully considered in the formulation design. On the other hand, the XPS measurements detected a Cl (2p) peak on samples after degradation treatment, confirming C-Cl bonds are generated. Furthermore, the ^{13}C-NMR measurements revealed that the methyl groups in the diene side chain are chlorinated. These chlorinated methyl groups increase the crosslinking density by reacting with other EPDM rubber molecules, consequently causing stiffening degradation, which leads to stress cracking, break-up, and flaking.

Acknowledgements

This work was supported in part by a Grant-in-Aid (21655080) for Chalenging Exploratory Research and Grant-in-Aid (223501000) for Scientific Research (B) from Japan Society for the Promotion of Science and JST-JICA SATREPS.

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