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Investigation of Fluoroelastomer Degradation in Simulated Severe Accident Environment of Nuclear Power Plants

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1. Introduction

After the accidents in Fukushima and Three Miles Island, the importance of maintaining the integrity of containment building has become more important. In SA, harsh environment was generated such as high temperature and radiation environment. The hydrogen was generated from reaction between damaged fuel and coolant. And the accumulated hydrogen burned to create a high temperature profile. Therefore, safety-related equipment to mitigate the effects of severe accident (SA) are required to perform safety function in 10CFR50.34(f). And the mitigation and prevention equipment must be designed to operate in SA environment. And equipment survivability (ES) should be ensured in events (earthquake, blackout, etc.) and SA environment (temperature, radiation, pressure) according to SECY-90-016 and SECY-93-087 in US.

In this study, degradation behavior of fluoroelastomer in simulated severe accident environment (radiation, temperature) were investigated. Fluoroelastomer was used in valve such as sealing material of safety-related equipment. To investigate the degradation effect in normal operation period and SA environment, irradiation test and accelerated thermal aging test and were conducted sequentially. The specimens were exposed to normal operating condition and simulated severe accident environment. And tensile test and hardness test were conducted. The Fourier Transform Infrared (FT-IR) analysis to investigate the change of molecular structure after the degradation.

2. Experiment

2.1 Degradation test

Irradiation test was conducted using gamma ray from Co^{60} with dose rate of 9 kGy/hr at the room temperature in the air. According to IEEE-323, total integrated dose rate was 2.0×10^5 Gy to simulate the normal operating condition. To simulate the SA radiation environment irradiation test was performed with total integrated dose of 2.2×10^6 Gy.

Accelerated thermal aging was conducted to simulate the thermal degradation in normal operating condition. Aging environment was determined by using Arrhenius equation. The thermal decomposition energy of fluoroelastomer used 1.09 eV. The aging was conducted at 140 ℃ for 176.10 hours to simulate the operating condition of 54.4 ℃ for 60 years as shown in table I.

TABLE I. Test conditions for accelerated thermal aging

Activation energy	Operation condition	Accelerated thermal aging temperature/time
1.09 eV	54.4 ℃ / 60 years	140 ℃ / 176.10 hours

During the SA, temperature of atmosphere at containment increase rapidly due to the hydrogen burn. In this situation, peak temperature and time were different depends on scenarios and location of equipment. To determine the conservative temperature profile, single profile was established using stored histogram method, as shown in black line in fig 1 [1]. The temperature profile in the degradation test of fluoroelastomer rubber seal in in emergency reactor depressurization valve (ERDV) was using through thermal lag analysis with consideration of heat loss in the atmosphere in previous study [2].

TABLE II. Test cases of irradiation and thermal aging test

	Normal operating condition		SA environment	
	Irradiation Test (R(N))	Accelerated Thermal aging (ATA)	Irradiation Test (R(SA))	Thermal degradation test (D(SA))
Case 1				O
Case 2			O	O
Case 3	O	O	O	O

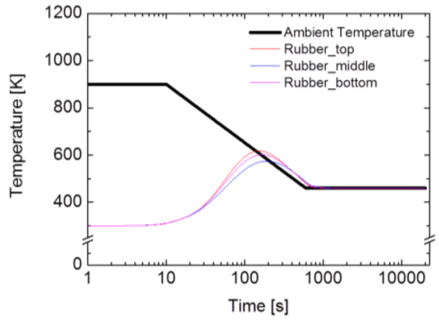

Figure 1. Exposure temperature profile of fluoroelastomer seal in ERDV (results of thermal lag analysis)

2.2 Characterization of Mechanical Properties

The mechanical properties of fluoroelastomer was measured using tensile test and hardness measurement. The elongation at break (EAB) and tensile strength (UTS) were measured. According to ASTM D412, the specimens were prepared type C, crosshead speed of 50 mm/min using a self-tightening grip and Instron 8801. And durometer shore A hardness were measured according to ASTM D2240.

2.3 Molecular structure analysis

The FT-IR analysis was performed to investigate the changes of structure and bonds caused by heat and radiation in normal operating condition and SA environment. The analysis mode was Attenuated total reflection (ATR) mode of FT-IR spectrometer (Nicolet iS50) with Ge crystal plate.

3. Results and discussion

3.1 Characterization of Mechanical Properties

The mechanical properties of polymeric materials are known to be influence by the radiation and heat. Therefore, according to ISO 37, the criteria of mechanical properties for elastomeric materials in the design basis event (DBE) environment is 50% of the initial properties at ISO 37. According to ISO 868, it also provides criteria for 10 changes in shore hardness. The degradation effects were evaluated by measuring mechanical properties such as EAB and UTS. The criteria are showed in blue and black line in figure 2 and 3 [2]. The hardness result of case 1 and reference were not significantly different, from 74.0 to 75.6. Irradiation effect of irradiation test of normal condition (R(N)) was not significant. The hardness was increased slightly in case 2 of the accelerated thermal aging in normal operating condition (ATA) after R(N). However, radiation effect in SA environment was significantly affected. Hardness increased to 96.1 and 96.9 in case 2, 3. The hardness decreases slightly after thermal degradation test in SA environment (D(SA)).

The results of tensile test with EAB and UTS as shown in figure 2. In normal operating condition, the EAB decreased from 427% to 209%. The EAB after the test of R(SA) in case 2 and 3 decreased to 39% and 041%, respectively. However, in the test performed only ATA case, it showed almost same value as the initial properties in reference case. Compared to the EAB, the UTS more susceptible to radiation. However, the effect of heat was not shown. Therefore, the effect of radiation was more significant than thermal effect.

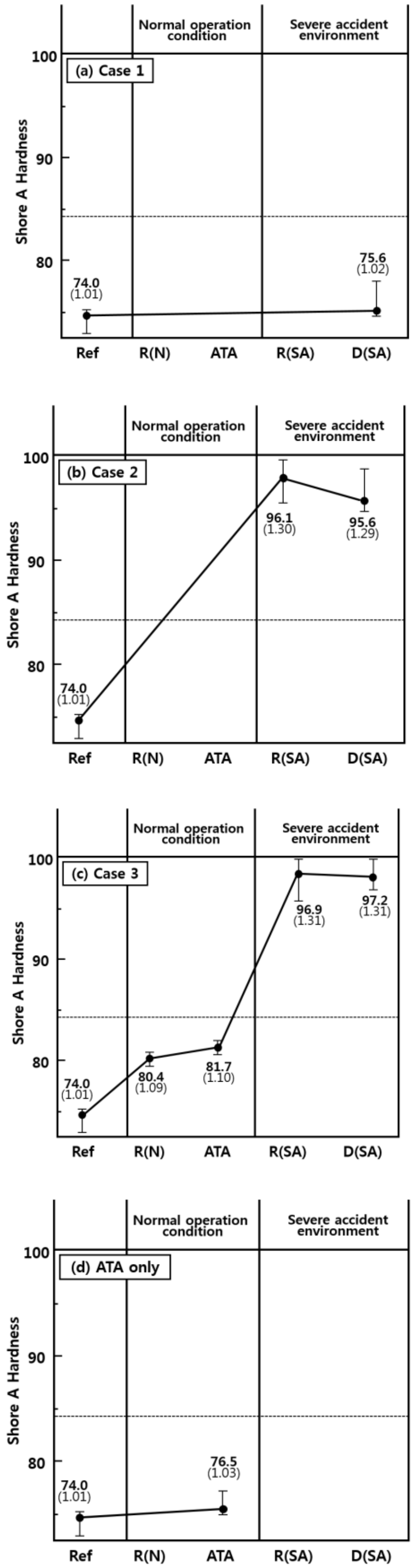

Figure 2. Results of hardness measurements of fluoroelastomer after the degradation test, (a) Case 1, (b) Case 2, (c) Case 3, and (d) Accelerated thermal aging only case [3]

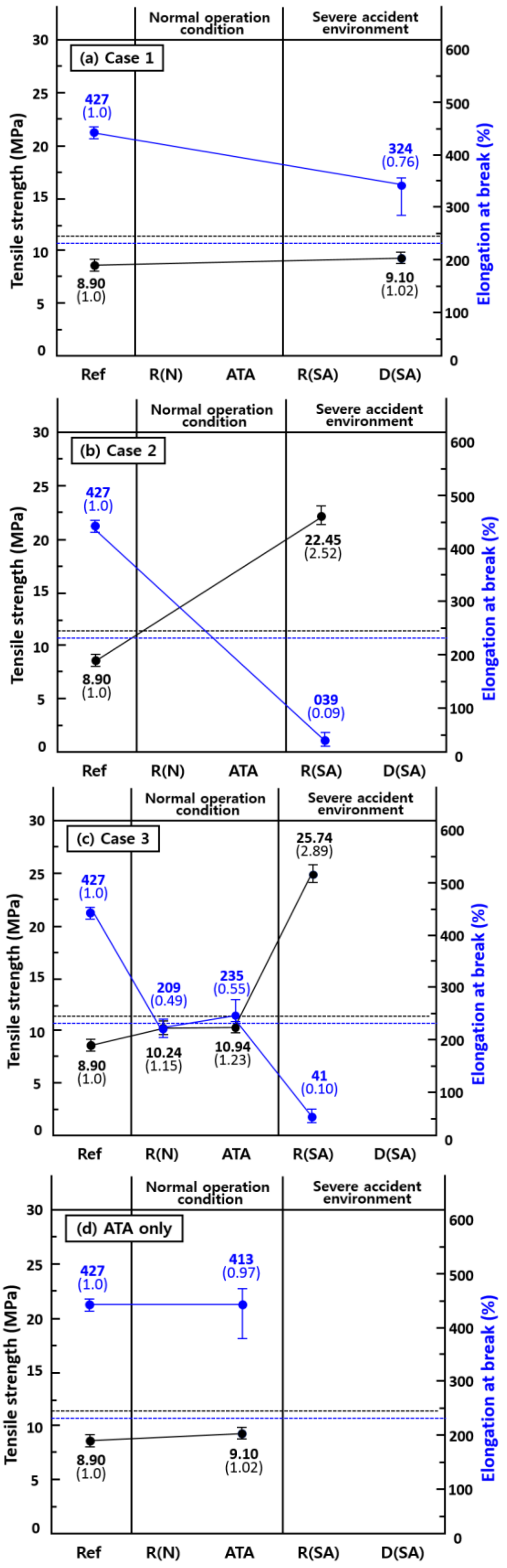

Figure 3. Results of tensile tests of fluoroelastomer after the degradation test, (a) Case 1, (b) Case 2, (c) Case 3, and (d) Accelerated thermal aging only case [3]

The mechanical properties of polymeric materials such as fluoroelastomer are influenced by the crosslink density. As the crosslinking occurs, the molecular bind to each other and difficult to move. Therefore, the hardness and UTS increase and the EAB decreases. In general, heat and radiation are known to increase the crosslinking of fluoroelastomer due to free radical generated from scission of bonds. Based on these experimental results, the effect of radiation is more severe than the thermal effect in SA environment to fluoroelastomer [3].

Shore hardness changed to less than 10 in the radiation and thermal aging environment under normal operation condition. And EAB and UTS also changed to less than 50% of initial properties. However, hardness, EAB, and UTS exceeded criteria after the irradiation test of SA environment. The SA temperature environment did not significantly affect the change of the mechanical properties of the fluoroelastomer. Based on these results it is considered that the SA radiation environment is significantly affect the integrity of the fluoroelastomer.

To assessment of equipment survivability of elastomer in SA environment, further consideration should be required to the geometry in which the elastomer is used and the minimum mechanical properties to perform the safety function. Therefore, criteria can not be used directly in the assessment of equipment survivability in SA environment. However, in this study, these criteria were used to evaluate the degradation behavior of normal operation condition of elastomers and to investigate the basic study for develop the criteria in the SA environment.

3.2 Molecular structure analysis

The broad and strong peak appeared at 882, 1100-1300 cm^{-1} indicates that the C-F bond in reference specimen. In addition, peaks at 750 and 820 cm^{-1} indicating C-H bonds appeared. In the case 1, FT-IR analysis result was almost similar to the reference as shown in fig. 4 (a). It was not significantly different from the reference case after the test exposed to the SA temperature environment. However, after the R(SA) in case 2, C=O peak at 1720 cm^{-1} was formed as shown in fig. 4 (b). The function groups in the molecular such as C-H, C-F were broken by radiation effect. C=O bond were formed by reacting with oxygen in atmosphere at this site. And scission of functional group generated free radicals. Crosslink increased due to formation of link between molecular structure by free radicals. The double bonds and crosslink density, such as C=O are known to affect the mechanical properties of polymeric materials [4]. After the D(SA), the peak intensity of C-F, C-H decreased significantly. The high temperature in D(SA) caused thermal decomposition and scission of main chain of the molecular structure of irradiated specimens. In the case 3, specimens exposed to a relatively low dose rate. The C-O was generated in this case as shown in fig. 4 (c). However, after the R(SA), peak of C-O as well as

C=O appeared. Therefore, radiation environment of SA affected the generation of C=O, which has a significant effect on the mechanical properties of the materials.

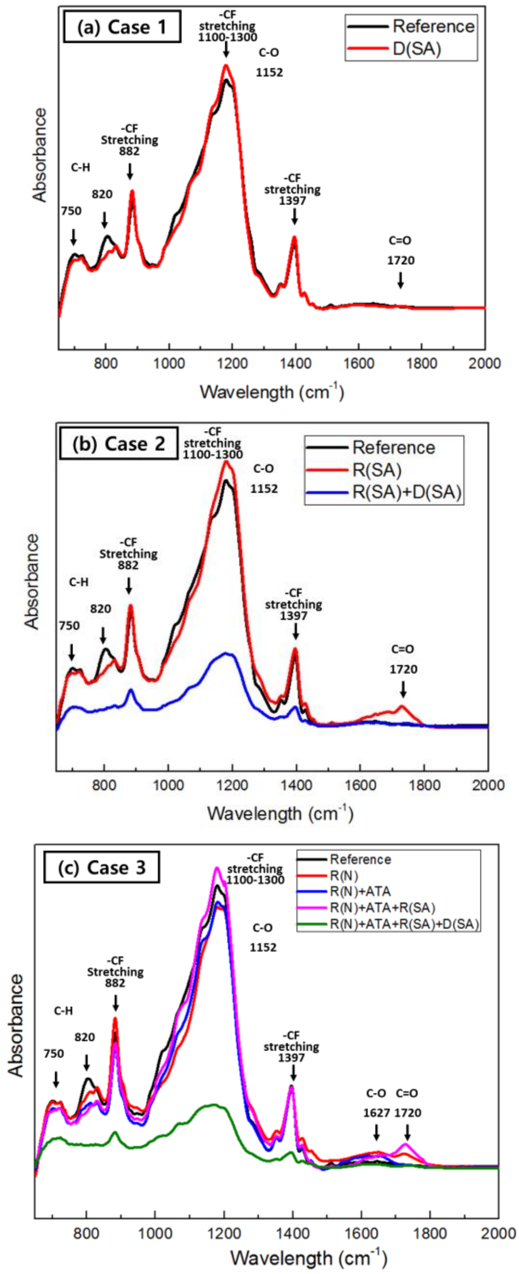

Figure 4. Results of FT-IR analysis of fluoroelastomer after the degradation test, (a) Case 1, (b) Case 2, and (c) Case 3 [2]

4. Conclusion

The degradation test and measurement of mechanical properties of fluoroelastomer were conducted to investigate the degradation effect of radiation and heat. The accelerated thermal aging was performed to simulate the normal operating condition. And thermal degradation test was conducted in SA temperature profile with thermal lag analysis. The total integrated dose rate was determined according to IEEE-323.

In the normal operating condition and SA environment, thermal effect did not significantly on hardness. The EAB and UTS was almost same as behavior of hardness during the test. The radiation effect on change of EAB and UTS during the test also significant. In radiation environment of normal operating condition and SA environment, C-O was formed by free radical from the broken bonding of molecular structure. And C=O was formed after the SA radiation environment. Thermal decomposition was generated during the thermal degradation in SA temperature environment.

Therefore, radiation caused oxidative degradation and forms C-O and C=O and these bonds are considered to have a significant influence on the mechanical properties. The thermal effect in the normal operating condition is not significant. However, thermal decomposition occurs in the SA environment, and the fluoroelastomer is predicted to be unable to perform the sealing function.

Compare to the criteria for the mechanical properties of the elastomer suggested in ISO 37 and 868, Under the normal operating condition, hardness, EAB, and UTS were not exceeded the criteria. However, after the test in SA radiation environment, fluoroelastomer were significantly degraded and exceeded criteria.

The investigation of degradation effect in radiation with various dose rate was required to further understand of degradation behavior of fluoroelastomer as the future work.

5. Acknowledgements

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