*Transactions of the Korean Nuclear Society Autumn Meeting*
*Yeosu, Korea, October 25-26, 2018*

# Investigation of Thermal Stability of Fluoroelastomer in Simulated Severe Accident Environment of Nuclear Power Plants

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## 1. Introduction

After severe accidents in Three Miles Island and Fukushima Daiichi, functionality of safety-related equipment to mitigate of accident effects has become more important in SA (severe accident) environment. In SA, high temperature and high dose radiation were generated. The hydrogen was generated form damaged fuel cladding and coolant water. And the hydrogen burned to create high temperature environment. Therefore, according to 10CFR50.34, SECY-90-016, and -93-087, safety-related equipment to prevent or mitigate the accident effects are must perform their functions in required period in SA environment (temperature, radiation, and pressure, etc.). [1]. Polymeric materials in safety-related equipment such as cable and valve are more vulnerable compare to metallic components in accident environment. Therefore, to ensure the survivability and functionality of safety-related equipment, the assessment of polymeric materials must be performed. Therefore, to investigation of degradation of polymeric materials is very important to ensure the safety of NPP. [2].

In this study, behavior of thermal stability of fluoroelastomer in normal operation condition and SA environment (heat, radiation) were investigated. Fluoroelastomer specimens are exposed to normal operation condition. Irradiation test and accelerated thermal aging were performed sequentially. And degradation test in irradiation test and SA temperature profile were conducted. To investigate the thermal stability behavior by thermogravimetric analysis (TGA) and the Fourier transformed infrared (FT-IR) spectroscopy was performed to investigate the change of molecular structure.

## 2. Experiment

Gamma-irradiation test was conducted with $Co^{60}$ and dose rate of 9 kGy/hr at the room temperature in the air. To simulate the radiation environment in normal operating condition, irradiation test was conducted with total integrated dose of 200 kGy. In case of SA environment, total dose rate in irradiation test was 2200 kGy, according to IEEE-323.

Accelerated thermal aging and thermal degradation test in SA temperature profile were conducted to simulate the heat condition of normal operating condition and SA environment. Test condition of accelerated thermal aging condition was determined by Arrhenius equation, maximum operating temperature, and operating period. The aging was conducted at 140 ℃ for 176.10 hours to simulate the operating condition of 54.4 ℃ for 60 years

In the SA environment, temperature of atmosphere at containment increase due to the hydrogen burn. To determine the temperature profile, single temperature profile was established by stored histogram method, as shown in black line in figure 1. The temperature profile of fluoroelastomer rubber seal in emergency reactor depressurization valve (ERDV) after thermal lag analysis was used for thermal degradation test.

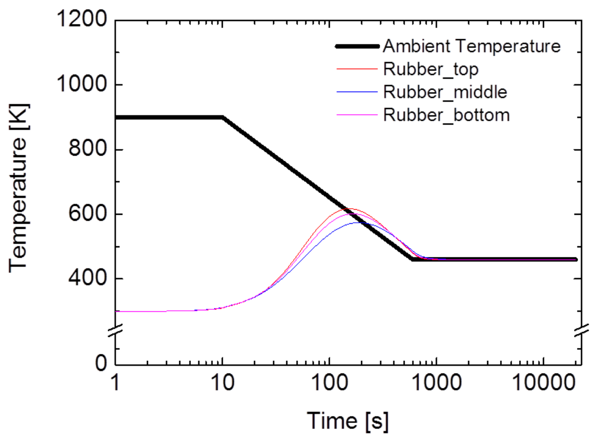



**Figure 1**. Exposure temperature profile of fluoroelastomer seal in ERDV (results of thermal lag analysis)

**TABLE I.** Test cases of irradiation and thermal aging test

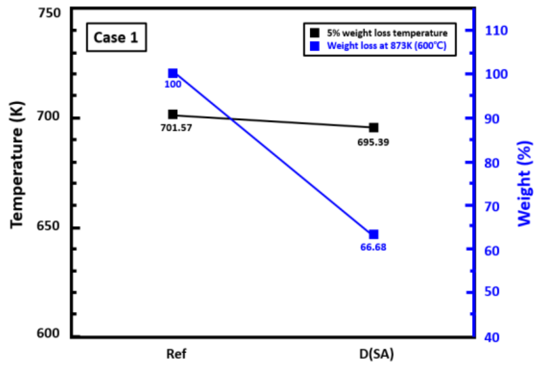
| | Normal operating condition | | SA environment | |
|---|---|---|---|---|
| | Irradiation Test (R(N)) | Accelerated Thermal aging (ATA) | Irradiation Test (R(SA)) | Thermal degradation test (D(SA)) |
| Case 1 | | | | O |
| Case 2 | | | O | O |
| Case 3 | O | O | O | O |

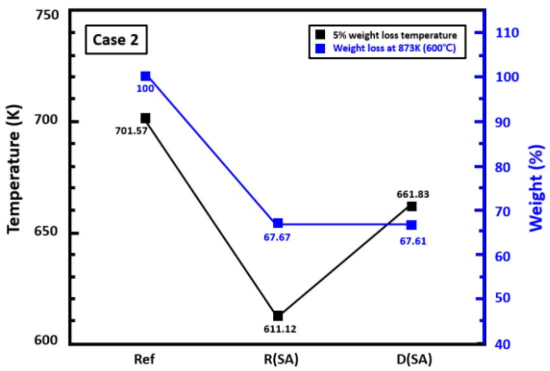
## 3. Results and discussion

### *3.1 Characterization of thermal properties*

Thermogravimetric analysis was conducted to investigate the thermal stability of fluoroelastomer in various cases. In early stage of degradation, the generation and release of volatile materials such as dehydrofluorination in the molecular are not significant. Therefore, in case 1, 5% weight loss temperature was similar to reference case. However, weight loss at 873K decreased dramatically to 66.68 %. Sufficient heat and time were supplied until 873K, and volatile materials was released from the molecular, so that the weight loss appears to be more severe than early stage degradation step. Thermal stability of irradiated fluoroelastomer in case 2 and 3 (R(SA)) drastically decreased. Based on these results after the irradiation, radiation in SA environment has the most significant effect on thermal stability. When heat was applied to irradiated fluoroelastomer, thermal stability increased. In this region, recrystallization can reform tie molecular which were broken by oxidation by oxidative in the air. [4].

Activation energy of thermal decomposition was calculated using 5% weight loss temperature in various heating rate (5, 10, 15, 20, and 30 ℃/min), and Flynn-Wall-Ozawa equation according to ASTM E1641. The activation energy measurement results are similar to the behavior of 5% weight loss temperature and weight loss at 873K.



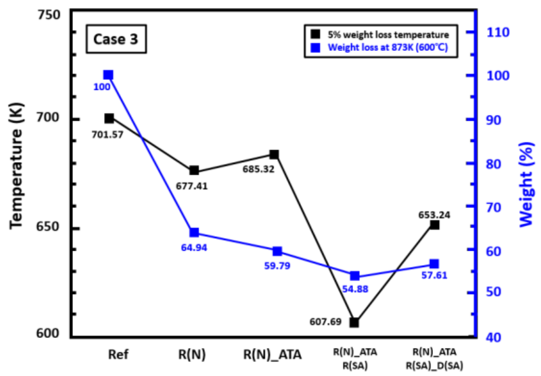




**Figure 2**. Results of thermogravimetric analysis of fluoroelastomer in normal operation and SA environment (5% weight loss temperature and weight loss at 873K)

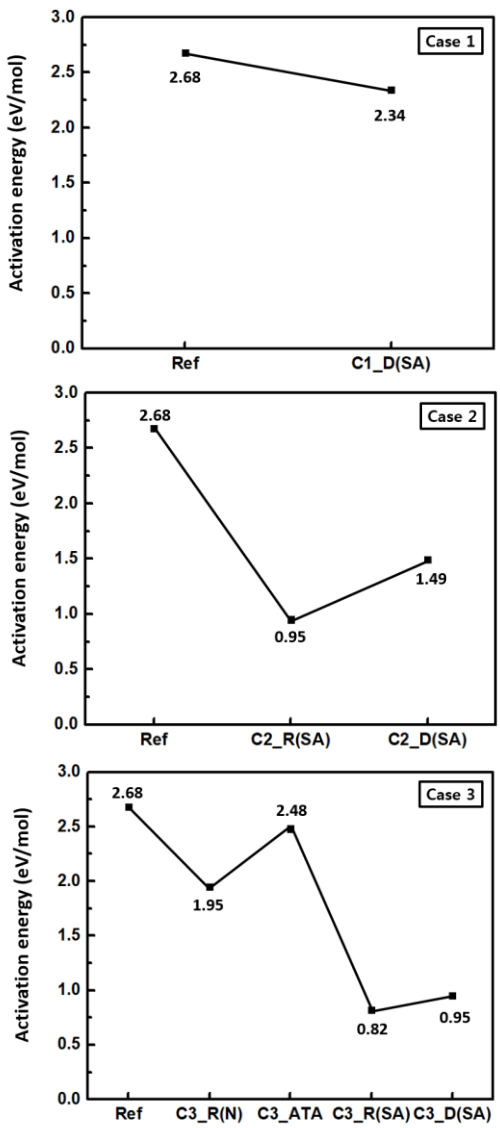



**Figure 3**. Results of thermal decomposing activation energy of fluoroelastomers in normal operation and SA environment

### *3.2 Molecular structure analysis*

FT-IR analysis was performed to investigate the change of molecular structure and chemical bonding caused by environmental factors (heat, radiation) in normal operating condition and SA environment. Attenuated total reflection (ATR) mode with Ge crystal plate used to analysis.

The peak with wide and strong intensity at 1100-1300 $cm^{-1}$ in reference case, indicate that the C-F bond in fluoroelastomer. And C-H bonds (750 and 820 $cm^{-1}$) appeared. After the degradation in SA environment without aging under normal operation condition (Case 1), almost similar to reference case. However, after the irradiation in case 2 and 3, C=O peak at 1720 $cm^{-1}$ was formed. The function group in the molecular such as C-H and C-F were scissioned by radiation and radicals in molecular were react with oxygen in the air. Based on these results, the decrease in thermal stability due to radiation is caused by formation C=O process. [5].

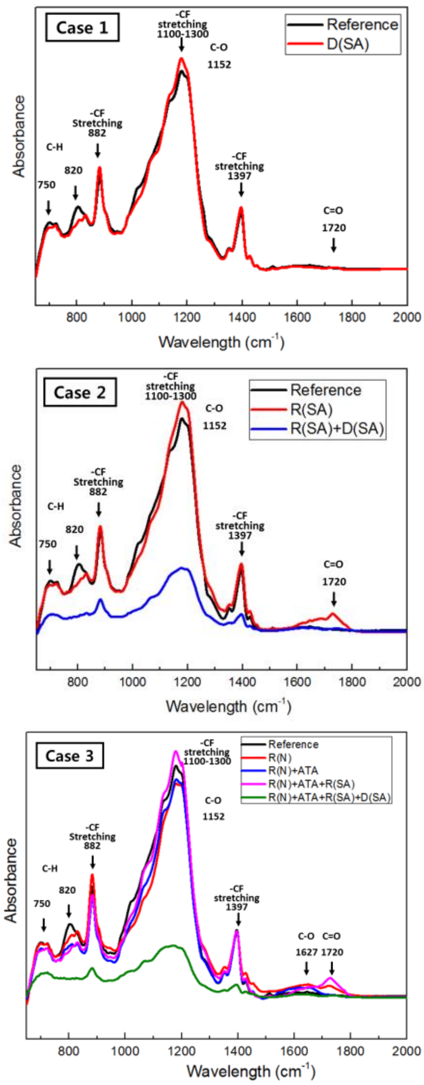



**Figure 4**. Results of FT-IR analysis in normal operation and SA environment

## 3. Conclusion

Degradation tests under simulated normal operation condition and SA environment were performed to investigate the thermal stability behavior of fluoroelastomer. And TGA and FT-IR analysis were conducted.

Based on analysis results of TGA and FT-IR, the fluoroelastomer showed a significant decrease in thermal stability due to radiation in SA environment. This degradation behavior is caused by the decreasing of the crystalline region due to the scission of molecular bonds and reaction with oxygen in the air during C=O formation process. After the accelerated thermal aging and thermal degradation on irradiated fluoroelastomer, decreased thermal stability due to the irradiation was restored. When heat is applied to the groin where the crystalline region is reduced due to oxidative degradation, the tie molecular is reformed and recrystallization is generated. Therefore, thermal stability increased by this annealed phenomenon.

The investigation of degradation behavior was required to further understand of degradation behavior of fluoroelastomer as the future work.

## ACKNOWLEDGMENTS

This work was financially supported by the Major Institutional Project of Korea Institute of Machinery and Materials (KIMM) funded by the Ministry of Science, ICT and Future Planning (MSIP). This work was also financially supported by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea Government Ministry of Trade Industry and Energy (MOTIE) (No. 20174030201430).

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