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# Effects of heat and gamma radiation on the degradation behaviour of fluoroelastomer in a simulated severe accident environment



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#### A R T I C L E I N F O

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### ABSTRACT

In this study, the effects of heat and radiation on the degradation behaviour of fluoroelastomer under simulated normal operation and a severe accident environment were investigated using sequential testing of gamma irradiation and thermal degradation. Tensile properties and Shore A hardness were measured, and thermogravimetric analysis was used to evaluate the degradation behaviour of fluoroelastomer. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to characterize the structural changes of the fluoroelastomer. Heat and radiation generated in nuclear power plant break and deform the chemical bonds, and fluoroelastomer exposed to these environments have decreased C–H and functional groups that contain oxygen and double bonds such as C–O, C=O and C=C were generated. These functional groups were formed by auto oxidation by reacting free radicals generated from the cleaved bond with oxygen in the atmosphere. In this auto oxidation reaction, crosslinks were generated where bonded to each other, and the mobility of molecules was decreased, and as a result, the fluoroelastomer was hardened. This hardening behaviour occurred more significantly in the severe accident environment than in the normal operation condition, and it was found that thermal stability decreased with the generation of unstable structures by crosslinking.

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1. Introduction

It is generally accepted that the probability of the occurrence of a severe accident (SA) in nuclear power plants (NPPs) is extremely low. However, the Three Mile Island and Fukushima accidents revealed that SAs should be treated as critical issues because their impacts are significant both socially and economically [1]. Following the accidents at Three Mile Island and Fukushima, the concept of the beyond design basis accident (BDBA) including SAs caused by unexpected natural disasters has become more important. To ensure the safety of NPPs and prevent the release of radioactive materials during a SA, the safety functions of the safety-

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related equipment need to be performed even in SA environments. For example, the equipment necessary to maintain the integrity of the containment must perform safety-related functions in a SA with hydrogen generated by the equivalent of 100% clad-water reaction. Likewise, mitigation and prevention equipment must be designed to operate in SA environments during the periods required for safe shutdown. Equipment survivability (ES) should therefore be ensured in various events (earthquake, blackout, etc.) and SA environments (pressure, temperature, radiation), according to SECY-90-016 and SECY-93-087. During a SA, high temperature, radiation, and pressure can be generated by the burning of gases from the fuel cladding and coolant interaction. Severe environments generated by hydrogen burning can cause significant damage to the integrity of the materials that make up the safety-related equipment. In particular, polymeric materials widely used in safety-related equipment are relatively vulnerable to severe environments [2,3]. Generally, free radicals are generated by scissioned

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chemical bonds in environments with high temperature and radiation in excess of the chemical bond energy. These free radicals react with other radicals, molecules, and oxygen in the atmosphere to form oxides and unstable molecules. Unstable molecular structures and radicals containing oxygen normally react with other molecules, resulting in degradation of polymeric materials. This phenomenon, called the auto-oxidation mechanism, has been reported as a major degradation mechanism causing the failure of polymer-based components and other polymeric mechanisms. The prediction of degradation behaviour, though, is highly difficult in the normal operation and accident environments of NPPs due to multiple degradation stressors, such as heat and radiation. To ensure the integrity and survivability of the safety-related equipment, degradation behaviour of polymers must be investigated in SA environments [3–7].

In this study, in order to investigate the effects of the heat and radiation of NPP environments on the material characteristics of fluoroelastomer (FKM), radiation and thermal tests were conducted to simulate both the normal operation condition and a SA environment. Considering the limitations in terms of the time and financial resources required to simulate both heat and radiation environments at the same time, the radiation and thermal degradation tests in this work were sequentially performed. Accelerated thermal aging and thermal degradation tests were performed to simulate the normal operation and SA environments, respectively. To evaluate the effect of radiation and heat on the degradation behaviour of fluoroelastomer, mechanical properties were analysed through tensile tests and Shore A hardness measurements, and the 5% weight loss temperature and thermal decomposition activation energy (E<sub>a</sub>) were obtained via thermogravimetric analysis (TGA). Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analysis were also conducted to investigate the changes in the chemical bonds of the molecular structure of fluoroelastomer.

#### 2. Experimental

#### 2.1. Materials

The fluoroelastomer in this work consists of a copolymer of vinylidene fluoride and hexafluoropropylene with a fluorine content of 66% and includes carbon black (15.95 wt%), zinc oxide (2.39 wt%), and magnesium oxide (0.80 wt%) as stabilizing agents, calcium hydroxide (0.80 wt%) as an acid acceptor agent, bis(2-ethylhexyl phthalate) (0.16 wt%) as a plasticizer, and bisphenol A (0.16 wt%) as a curing agent. Fluoroelastomer specimens were shaped into ASTM D412 type C for the accelerated thermal aging and characterization [8].

#### 2.2. Degradation test

Accelerated thermal aging treatment was performed to simulate thermal degradation in the normal operating condition using the Arrhenius equation, as shown in Eq. (1),

$$\boldsymbol{t}_2 = \boldsymbol{t}_1 \, \boldsymbol{e} \boldsymbol{x} \boldsymbol{p} \, \left\{ \frac{\boldsymbol{E}_a}{\boldsymbol{k}} \left( \frac{1}{\boldsymbol{T}_2} - \frac{1}{\boldsymbol{T}_1} \right) \right\},\tag{1}$$

where  $t_1$  is the operation time (h),  $t_2$  is the accelerated thermal aging time (h),  $T_1$  is the operation temperature (K),  $T_2$  is the accelerated thermal aging temperature (K), *K* is the Boltzmann constant (8.62\*10<sup>-5</sup> eV/K), and  $E_a$  is the thermal decomposition activation energy (eV). The  $E_a$  of the fluoroelastomer was calculated according to the Flynn–Wall–Ozawa method of ASTM E1641, as shown in Eq. (2) [9],

$$\boldsymbol{E}_{\boldsymbol{a}} = \frac{\left(\frac{\boldsymbol{K}}{\boldsymbol{b}}\right) \Delta \log[\boldsymbol{\beta}]}{\Delta(\frac{1}{\boldsymbol{I}})},\tag{2}$$

where *K* is the Boltzmann constant (8.62\*10<sup>-5</sup> eV/K), *b* is assumed as 0.457.  $\beta$  is the heat rate (K/min), and T is the 5% weight loss temperature (K). The 5% weight loss temperature was measured at various heating rates (5, 10, 15, and 20 °C/min), and the E<sub>a</sub> of the fluoroelastomer was calculated to 1.09 eV. Accelerated thermal aging was conducted at 140 °C for 176.10 h to simulate the operation conditions of the fluoroelastomer seal in the emergency reactor depressurization valve (ERDV) at 54.4 °C for 60 years. The accelerated thermal aging temperature was determined as the temperature at which the weight did not change in the thermogravimetric curve of the non-aged fluoroelastomer. Table 1 shows the environmental conditions for accelerated thermal aging. Gamma irradiation was carried out using <sup>60</sup>Co with a dose rate of 9 kGy/hr at room temperature in the atmospheric air. In the preaging stage, irradiation was performed at 200 kGy according to IEEE-323. To simulate the radiation environment of a SA, a total integrated dose of 2000 kGy was used in the irradiation tests [10,11]. In a SA environment, hydrogen burn can occur in the atmosphere of the containment building by the accumulation of hydrogen over the low explosive limit generated from the interaction between high-temperature fuel cladding materials and coolant. In a hydrogen burn situation, the temperature of the atmosphere in the containment building increases rapidly. However, the environment generated by a hydrogen burn differs in each accident scenario, such as peak temperature and peak time, making it difficult to predict all accident scenarios. Therefore, a single temperature profile was derived to simulate the SA temperature profile using the stored histogram method, as shown in Fig. 1. Using this SA temperature profile, the exposure temperature of the fluoroelastomer rubber seal in the ERDV was predicted by analysis that considers the thermal lag between atmospheric air and the surface of the fluoroelastomer seal [1,10–14]. Table 2 lists the test conditions to investigate the effect of heat and radiation in the normal operating condition and SA environment. In case 1, only the thermal degradation test under the SA environment [D(SA)] was conducted. In case 2, to simulate radiation in the SA environment, the gamma irradiation test [R(SA)] and the thermal degradation test [D(SA)] were performed sequentially. In case 3, to simulate the normal operation condition, the fluoroelastomer specimen was exposed to a pre-aging environment, namely radiation [R(N)] and accelerated thermal aging (ATA) tests, and then exposed to the SA environment.

#### 2.3. Mechanical properties

The specimen was designed according to ASTM D412 type C. The tensile testing was carried out with an Instron 8801 system at a crosshead displacement speed of 50 mm/min at room temperature using a self-tightening eccentric roller grip. Shore A hardness measurements and tensile tests were performed according to ASTM D2240 and ASTM D412 [8,13].

#### 2.4. Thermal properties

First, 5–20 mg of fluoroelastomer specimen powder was prepared for TGA using a TA Q500 at 25–627 °C with a heating rate of 10 °C/min in nitrogen. Through the TGA, the 5% weight loss temperature and the maximum temperature of the weight loss rate of the fluoroelastomer were obtained.

#### Table 1

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Accelerated thermal	$2\sigma_{1}\sigma_{1}\sigma_{2}\sigma_{1}\sigma_{2}\sigma_{1}\sigma_{2}\sigma_{1}\sigma_{2}\sigma_{2}\sigma_{1}\sigma_{2}\sigma_{2}\sigma_{2}\sigma_{2}\sigma_{2}\sigma_{2}\sigma_{2}\sigma_{2$	to similiate the h	ormal operation (	condition
	azine condition	to simulate the h	ormai obcration	condition.

Activation energy	Normal operation condition	Accelerated thermal aging condition
1.09 eV	54.4 °C	140 °C
	/ 60 years	/ 176.10 h



**Fig. 1.** Exposure temperature profile of the fluoroelastomer seal in the ERDV. The temperature of the FKM seal in the ERDV was analyzed considering the thermal lag between atmospheric air in the containment building and the seal [10,11].

#### 2.5. Structure analysis

FT-IR absorbance spectra were collected using a Nicolet iS50 with a germanium attenuated total reflectance attachment. The analysis was performed between 650 and 2000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and an accumulation of four scans. The XPS analysis was performed using an ultra-high vacuum system, a Thermo Fisher Scientific ESCALAB 250XI monochromated Al-K $\alpha$  X-ray source.

#### 3. Results and discussion

#### 3.1. Mechanical and thermal properties

The mechanical properties of polymeric materials are known to be significantly affected by heat and radiation. The degradation effects were investigated in terms of tensile properties including elongation at break (EAB) and ultimate tensile strength (UTS), as shown in Fig. 2. In case 1, the D(SA) testing condition with only SA

#### a (a) Tensile Strength (b) the strength (c) Tensile Strength (c) Tensile Strength (c) Case 1 (c) Case 2 (c) Case 3 (c)



Fig. 2. Results of fluoroelastomer tensile tests after the degradation tests: (a) tensile strength, and (b) elongation at break.

#### Table 2

Test cases for the irradiation and thermal aging tests.

	6.6			
Degradation	Pre-aging environment (normal operation)		Severe accident environment	
condition	Gamma irradiation [R(N)]	Accelerated thermal aging (ATA)	Gamma irradiation [R(SA)]	Thermal degradation test [D(SA)]
	Total irradiation dose is 200 kGy with 9 kGy/hr in the atmospheric air	Accelerated thermal aging is conducted at 140°C for 176.10 h to simulate the operation condition of 54.4°C and 60 years	Total irradiation dose is 2000 kGy with 9 kGy/hr in the atmospheric air	Temperature profile for equipment survivability (Fig. 1)
Case 1 Case 2 Case 3	$\begin{array}{l} D(SA) \mbox{ only } \\ R(SA) \rightarrow D(SA) \\ R(N) \rightarrow ATA \rightarrow R(SA) \rightarrow D(SA) \end{array}$			



Fig. 3. Results of the fluoroelastomer hardness measurements after the degradation tests.

temperature profile, there were no significant changes compared to other cases. In case 2, the tensile properties of the fluoroelastomer specimens changed significantly in the R(SA) test condition of SA radiation with 2000 kGy of gamma irradiation. After the thermal degradation in D(SA), tensile tests were not conducted because of specimen breakage. In case 3, tests were performed involving preaging in the normal operation condition of R(N) and ATA, followed by the severe accident environment of R(SA) and D(SA). Although there was no significant change in the mechanical properties under the normal operation condition, severe degradation occurred in which the mechanical properties changed significantly after the radiation condition of the severe accident environment. As shown in Fig. 3, EAB decreased to 41%, and the hardness increased to 97 in R(SA). This hardening behaviour also occurred in R(SA) of case 2, where the EAB decreased to 39%, and hardness increased to 96. The hardening behaviour is predominant in the degradation in R(SA), and the resulting change in mechanical properties was also the most severe. From these results, the hardening effects of the



Fig. 4. Thermogravimetric analysis results of the fluoroelastomer specimen 5% weight loss temperature.



Fig. 5. Results of the fluoroelastomer specimen temperature of maximum mass loss rate after the degradation tests.

fluoroelastomer specimens indicate that the molecules were crosslinked by the degradation stressors. Chemical bonds in the molecules were scissioned by heat and radiation, and free radicals were generated from these scissioned chemical bonds. The molecules containing unstable radicals and scissioned chemical bonds were then crosslinked with other molecules and free radicals. As a result of crosslinking, meaning the linking between molecular structures and other molecules in the network structure, stretching became difficult, i.e., material hardening occurred. These phenomena were accelerated by peroxides and oxidized free radicals due to oxygen in the atmosphere. TGA was conducted to investigate the thermal property behaviour and effect of environmental factors in normal operation and the SA environment, as shown in Figs. 4 and 5. The 5% weight loss temperature and the temperature of maximum mass loss rate measured by TGA showed a similar behaviour as the mechanical properties. The 5% weight loss temperature measured in case 1 represented a non-significant change;



Fig. 6. Thermal decomposition activation energy of the fluoroelastomer specimens after the degradation tests.



Scheme 1. General stages of the auto-oxidation mechanism [12].

however, following R(SA), this decreased significantly in cases 2 and 3. The behaviour of the temperature of maximum mass loss rate also changed significantly in R(SA). These thermal properties were affected dominantly by the R(SA) test condition. Using the TGA results, the thermal decomposition energies were calculated, as shown in Fig. 6. In the R(SA) condition, the  $E_a$  values were significantly decreased. The decreasing of  $E_a$  is evidence that an auto-oxidation reaction occurred by mechanisms such as thermosoxidation, chain scission, and crosslinking. C-H bonds are cleaved by thermal energy and irradiation, local chain scission and crosslinking are accelerated by oxygen supplied from atmospheric air, and volatilization is activated in the polymer chains. Therefore, the weight loss is accelerated, and  $E_a$  from the thermogravimetric curve decreases as degradation progresses. It was found that  $E_a$  decreased under irradiation conditions such as R(N) and R(SA) and then increased in ATA and D(SA). At elevated temperature, molecular partial melting and mobility increased due to the annealing that recrystallized to form a stable structure and the decrease of radicals. In addition, in the thermal degradation condition, the diffusion path for oxygen penetration to the fluoroelastomer is limited. On the contrary, it is considered that the formation of radicals generated by chemical bond scission, which acts along the diffusion path of oxygen, occurred relative to the inside of the fluoroelastomer [15–17]. Based on these results, the behaviour of the thermal properties of the fluoroelastomer specimens was also affected by crosslinking. Crosslinked radicals and molecules generated unstable regions and phases in the polymeric system. The formation of these unstable regions affected an increase in the interface region between the molecules or phases, which led to oxygen penetration paths and the generation of molecular end-groups and other radical generation sites. As a result of these phenomena, the thermal stability of the polymeric system decreased [18–20].

#### 3.2. Structure analysis

The auto-oxidation degradation mechanism includes initiation, propagation, chain branching, and termination stages, as shown in

Scheme 1. In basic auto-oxidation, hydrogen is abstracted in the initiation stage by an initiator such as heat or radiation. In the propagation stage, hydrogen is abstracted by peroxyl radicals  $(ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet})$ . Free radicals generated by the hydrogen abstraction react with other radicals and polymeric structures in the branching and termination stages, forming molecular structures containing double bonds and oxygen. From this process, crosslinked molecules, double bonds, and oxidized chemical bonds (C=C, C-O, and C=O) are formed in the polymeric system. These structures have different molecular weights and are unstable due to random crosslinking and end-chain termination. Such characteristics consequently act as a factor affecting the crystallinity and mechanical properties of the polymer. FT-IR analysis was performed to identify changes in the molecular and chemical bonds [21,22]. As shown in Fig. 7, broad and strong peaks appeared at 882 and 1100–1300 cm<sup>-1</sup>, indicating C–F bonds, as well as peaks at wavelengths of 750 and 820 cm<sup>-1</sup>, indicating C–H bonds in the reference case. For case 1, the FT-IR analysis result was mostly similar to the reference. However, in the R(SA) condition in case 2, the C–H and C–F peaks decreased, while the C=O peak at 1720 cm<sup>-1</sup> increased, as shown in Fig. 7 (b). Free radicals generated by scissioned C–H and C–F bonds due to the high energy radiation reacted with oxygen in the atmosphere to form C=O bonds. The C=O bond peak may be evidence of the auto-oxidation mechanism. Following D(SA), the peak intensity of the C-H and C-F bonds decreased significantly. At high temperatures, such as in a SA environment, polymeric materials undergo thermal decomposition and main chain scission following irradiation. In case 3, the C=C bond peak increased in the R(N) condition, as shown in Fig. 7 (c). In this step, due to the irradiation, the bond chains were scissioned and oxidized. After D(SA) in case 3, the C=C bonds changed to C=O due to the auto-oxidation mechanism. Chemical bonds in the molecules were scissioned by irradiation, and hydrogen from the scissioned chemical bonds in the molecules reacted with other bonds in the molecules, forming unsaturated double bonds such as C=C and C=O, a process that has a significant effect on the mechanical and thermal properties of polymeric materials [23–25].



Fig. 7. FT-IR spectra of the fluoroelastomer specimens after degradation tests for (a) Case 1, (b) Case 2, and (c) Case 3.



Binding Energy (eV)

Fig. 8. XPS spectra of the fluoroelastomer specimens after degradation tests for (a) Case 1, (b) Case 2, and (c) Case 3.

The XPS analysis was then performed to investigate the oxidation behaviour on the surface area of the fluoroelastomer under various environments, as shown in Fig. 8. In case 1 [D(SA)], following thermal degradation, the number of C-C/C-H bonds decreased, while that of the C–O, C=O, and CF<sub>3</sub> bonds increased. In this stage, heat under the SA environment acts as the initiator to scission the C-C and C-H bonds. The C-O and C=O chemical bonds containing oxygen are generated by reactions between the scissioned ends of the molecular chains and oxygen in the atmosphere. The number of CF<sub>2</sub> bonds slightly increased from the combination of CF<sub>2</sub> and F radicals generated by the CF<sub>3</sub> and CF<sub>2</sub> scission. In contrast, the effects of radiation under the SA environment were slightly different. In cases 2 and 3, the intensity of the C-C/C-H bonds decreased significantly, indicating that scissions of the branch and main chains occurred in the molecular structure. In addition, the peak intensity of CF2 increased, which indicates that free radicals containing fluorine from the scission of CF<sub>2</sub> and CF<sub>3</sub> reacted with the sites of CF<sub>2</sub> and CH scission in the molecular structure, resulting in an increase in CF<sub>3</sub> bond intensity. In the case of thermally degraded fluoroelastomer after irradiation under the SA environment, the C–O and C=O bond intensity decreased. This post-irradiated annealing phenomenon was also observed in the mechanical and thermal property measurements and  $E_a$  calculation results. While the mechanism of post-irradiated annealing is not fully understood, the free radicals and unstable structure by irradiation in the crystalline region have a higher mobility at high temperatures with thermal degradation under a SA and are therefore thought to form bonds with C or H at the interfaces between amorphous regions or recombine into stable molecular chains. Because of this annealing mechanism, the thermally degraded specimen under the SA condition after R(SA) exhibited a decrease in the peak intensity of the oxidized chemical bonds (C-O, C=O) in the molecular structure, a decrease in  $CF_3$  generated by irradiation, and an increase in CF<sub>2</sub>, as observed through XPS spectra [26–28]. Degradation by heat and radiation under the normal operation condition [R(N), ATA] did not significantly affect the molecular structure changes under the SA environment or the mechanical and thermal properties, while aging under the normal operation condition did not affect the degradation behaviour under the SA environment [29-33].

Ongoing studies are aimed at investigating the radiation, thermal, and humidity effects in a more detailed degradation process of fluoroelastomer, along with analysis of the comprehensive compatibility and survivability of fluoroelastomer under various environmental factors in NPP severe accidents. Further, the diffusion-limited oxidation effect on fluoroelastomeric components will also be studied.

#### 4. Conclusion

The objective of the present work was to investigate the effects of heat and radiation on the degradation behaviour of fluoroelastomer under normal operation and a SA environment. Fluoroelastomer samples were sequentially exposed to radiation and heat under a simulated environment, and measurements of mechanical and thermal properties were conducted through tensile tests, hardness measurements, and TGA. Molecular structure analysis was performed via FT-IR and XPS.

In case 1, the mechanical properties of specimens exposed only to SA thermal degradation did not significantly change. The thermal properties and  $E_a$  in this case did not change significantly either compared to other cases. This is because the free radical and autooxidation reaction did not proceed due to insufficient energy for chemical bond scission in the molecular structure. In the molecular analysis, it was found that the intensity of the C–C/C–H bonds decreased, and oxidized bonds such as C-O and C=O were observed but did not significantly affect the properties of the specimen. However, in cases 2 and 3 with the R(SA) test condition, the C-O and C=O bonds increased following irradiation. And polymer chains containing radicals generated by the autooxidation reaction were linked due to the high reactivity of the radical site. Crosslinked polymer chains have low mobility and limited elongation due to crosslinked bonding, resulting in decreased EAB and increased hardness. As a result, the crosslinked fluoroelastomer specimens were significantly hardened, and the thermal stability decreased due to the formation of unstable structures by auto-oxidation. In case 3, degradation under the normal operation condition did not significantly affect the degradation behaviour under the SA environment. The mechanical and thermal properties of the thermally degraded specimens after irradiation were restored by post-irradiation annealing. In this annealing process, the mobility of the free radicals and unstable structures increased at high temperature, leading to recombination with C or H radicals and recrystallization, which resulted in an increased thermal stability and  $E_a$ . In conclusion, fluoroelastomer was observed to show severe degradation behaviour in R(SA), which mimics the radiation environment of a severe accident. The survivability of fluoroelastomer under an NPP SA is dominantly affected by the radiation dose, which should be considered to ensure the equipment survivability of the safety-related equipment that include fluoroelastomer components.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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