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A STUDY ON THE AGING DEGRADATION OF ETHYLENE-PROPYLENE-DIENE MONOMER (EPDM) UNDER LOCA CONDITION

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The aging degradation and lifetime assessment of a domestic class 1E Ethylene-Propylene-Diene-Monomer (EPDM), which is a popular insulating elastomer for electrical cables in the nuclear power plants, were studied for equipment qualification verification under the Loss of Coolant Accident (LOCA) conditions. The specimens were acceleratively aged, underwent a LOCA environment, as well as tested mechanically, thermo-gravimetrically, and spectroscopically according to the American Society of the Testing of Materials (ASTM) procedures.

The tensile test results revealed that the elongation at break gradually decreased with an increasing aging temperature. The lifetime of EPDM aged isothermally at 140ºC was 1,316 hours and reduced to 1,120 hours after experiencing the severe accident test. The activation energies of the elongation reduction were 1.10 ± 0.196 eV and 0.93 ± 0.191 eV before and after the LOCA condition, respectively. The TGA test results also showed that the activation energy of the aging decomposition decreased from 1.35 eV to 1.02 eV after undergoing the LOCA environment. Although the mechanical property changes were discernibly observed during the aging process, along with the LOCA simulation, the FT-IR analysis showed that the spectroscopic peaks and their intensities did not alter significantly. Therefore, it can be concluded that the degradation of the domestic class 1E EPDM due to aging can be tolerable, even in severe accident conditions such as LOCA, and thus it qualifies as a suitable insulating material for electrical cables in the nuclear power plants.

KEYWORDS : EPDM, Thermal Aging, Degradation, LOCA, Activation Energy, Tensile Test

1. INTRODUCTION

One of the most prominent issues related to the safety of current nuclear power plants is the aging degradation of their parts and equipment because they have been operating for at least a couple of decades. In actuality, a nuclear power plant consists of more than a million parts and equipment. Among the numerous constituents, the most sensitive parts to the aging process are non-metallic substances, such as polymerized compounds. Power cables, signal cables, and control cables, which make up 95% of the electrical cables in the nuclear power plants, are made of polymers and elastomers. Therefore, even normal operation could be seriously at risk if some of the cables are critically damaged or degraded.

In fact, the performance of the electrical cables critically depends on the mechanical and physical integrity of the insulators since micro-cracks can threaten the loss of its insulating characteristics. Lengthy operation of nuclear power plants, especially those in a harsh environment, can induce the mechanical integrity degradation of the elastomers.

Due to its excellent properties, such as nil electrical conductivity, rubber-like flexibility, and outstanding weathering ability, Ethylene-Propylene-Diene Monomer (EPDM) has been widely used as an insulator material for electrical cables [1-3]. In nuclear power plants, only the upgraded class of 1E EPDM is used because of IEEE regulations that state that cables and joint parts should operate normally, even under a LOCA condition [4].

It is well-known that temperature and radiation are the most crucial environmental factors affecting the aging of the polymers. Furthermore, postulated accidents, such as Loss of Coolant Accident (LOCA), in which ambient temperature and pressure abruptly increase, can accelerate the deterioration of the insulator components that were

already degraded due to the extended operation. For these reasons, evaluating the aging degradation of the insulator is quite important to ensure its soundness and to predict the remaining lifetime following the operation's history, including the postulated accident situation.

Previous research has mainly focused on the synthesis and its mechanical properties [5], on the influences of ozone, UV light, ultrasonic irradiation, and ionizing radiation [6-8], on the thermo-oxidation [9-12], and on the effect of oxygen uptake under isothermal and isobaric conditions [13]. In the meantime, there has been little research on the performance of EPDM in relation to the equipment qualification and the nuclear safety, especially under a LOCA environment.

Therefore, in this study, experimental investigation was carried out in order to evaluate the aging degradation and lifetime of a domestic class 1E EPDM both with and without undergoing LOCA environment. Specimens were supplied by L domestic company.

2. EXPERIMENTAL

In order to estimate the thermal lifetime of EPDM experiencing a LOCA environment, serial experiments were carried out, as shown in Fig. 1. First, tensile test specimens were prepared and accelerative aging temperatures were determined to be 140ºC, 155ºC, and 170ºC after careful examination of its thermo-physical properties. In actuality, the temperatures seem to be relatively high, but even 170ºC is below the minimum temperature at which the physical and mechanical stability of the material can change.

After accelerative aging for up to 2000 hours, one batch of the specimens was tensile tested or thermo-gravimetrically analyzed, while another batch of the specimens was loaded in the LOCA chamber to be placed in the LOCA environment. In fact, tensile tests were conducted to measure the changes of elongation since the degree of elongation is one of the mechanical integrity indicators for aging elastomer materials. On the other hand, information on the decomposition kinetics due to aging can be provided by a Thermo-Gravimetric Analyzer (TGA) test.The specimens that experienced the LOCA condition were also tensile-tested or thermo-gravimetrically analyzed in order to examine the elongation or the decomposition and to compare the results before and after the LOCA test. Finally, Fourier Transformed Infra-Red (FT-IR) spectroscopic analyses analyzed the micro-structural changes of the aged specimens.

2.1 Tensile Test Using Universal Testing Machine

Tensile tests were carried out by a universal testing machine (model 5582, Instron Co.) in order to measure the

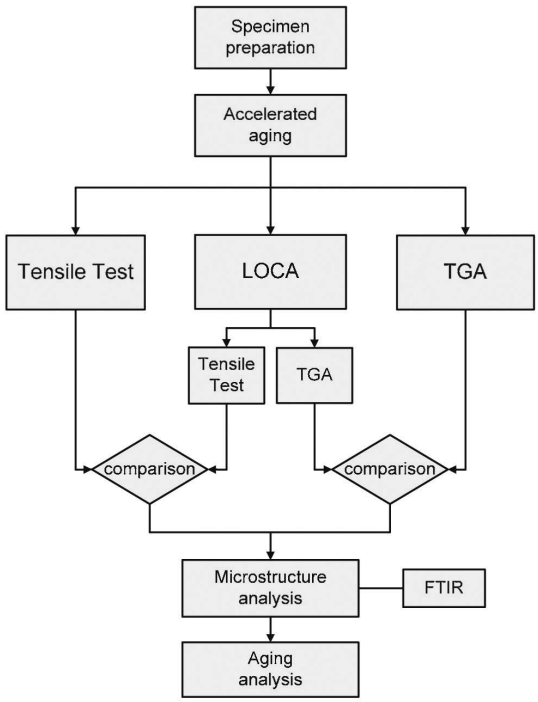
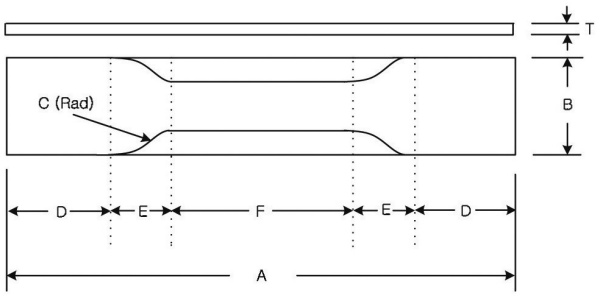


Fig. 1. Flow Chart of Experimental Procedure

elongation of the aged specimens. Test data were acquired through an in-situ PC data acquisition system that used Merlin software supplied by Instron Co. Measurements were conducted in a room temperature of 23 ± 2ºC, a humidity of 50 ± 5%, and a strain rate of 500 mm/min. The dimension of the specimen is shown in Fig. 2 and Table 1 shows its composition. Detailed tensile test procedures and parameters followed ASTM D412 [14].

Lifetime analysis was conducted based on the 60% elongation rule, which is generally accepted in the industry.



Dimension	A	B	C	D	E	F	T
Size (mm)	115	20	14	27	14	33	2

Fig. 2. Dimension of Test Specimen

Table 1. Composition of Class 1E EPDM Tested in this Study

EN-2		
Materials	Compounds(Product)	Ratio(%)
Base Polymer	EP 3/22 (Dupont)	48.3
Filler	TS-37 (Engel Hand)	31.8
Processing aids		1.5
Antioxidants		2.2
Stabilizer		5.1
Cross-linking coagents		5.7
Process Oil	(Shell)	2.5
Cross-linking agents		2.9
Total		100

In order to obtain the data, reproducibility tensile tests were repeatedly carried out with at least three specimens undergoing the same aging history.

2.2 Thermo-Gravimetric Analyzer Test

Thermal decomposition analysis was carried out using the TGA apparatus (model Q-500, Shimadzu Co.) under a nitrogen atmosphere. Specimens were heated from the ambient temperature to a required temperature of 800ºC with heating rates of 5, 10, 15, and 20ºC/min. 20 mg of EPDM specimens was used in the current tests and a dumbbell type thermocouple (Pt-Pt-10% rhodium) was used for the temperature control and measurements. Detailed experimental procedures followed ASTM E1641 [15].

2.3 Loss of Coolant Accident Test

The LOCA test was conducted following IEEE-383 [4] in the test facility at the Korea Institute of Machinery and Manufacturing (KIMM) in Daejeon, South Korea. A schematic diagram of the LOCA-MSLB (Main Steam Line Break) test loop is shown in Fig. 3.

The test temperature and pressure transients followed the LOCA profile of YGN units 3&4. However, as shown in Fig. 4, completing the original LOCA profile requires 182 days, which demands extensive man hours and material resources. Thus, in order to avoid the excessive resource consumption without losing technical justification, a new accelerated T-P profile was determined according to the accelerated thermal aging theory [16]:

$$t_1 = t_2 e^{[(E_a/k)(1/T_1 - 1/T_2)]} \quad (1)$$

where k is the Boltzmann's constant, E_a is the activation energy in eV, t is the time in sec, and T is the absolute temperature in K. The conservative modification resulted in reducing the test duration from 182 days to 4 days.

The activation energy for the modification in Equation (1) was taken from the activation energy obtained from the previous tensile test and a safety margin was added to the initial profile based on IEEE-383 [4]. Fig. 4 shows the modified LOCA profiles of the temperature and pressure, in which the whole test takes four days. As shown in the figure, the temperature and the pressure increase drastically at the initial stage and then stayed at 106.53ºC 6.6 hours later and at 1.25 atm 7 hours later, respectively. Specimens were loaded to the mandrel placed at the center of the test chamber (diameter 80 cm × length 200 cm). The temperature and pressure in the chamber were controlled by an automatic control system and chemical water consisting of 3,000 ppm boron and 0.28 mol sodium hydroxide, which were sprayed over specimens during the test according to the LOCA test specification for Equipment Qualification (EQ) [17-18].

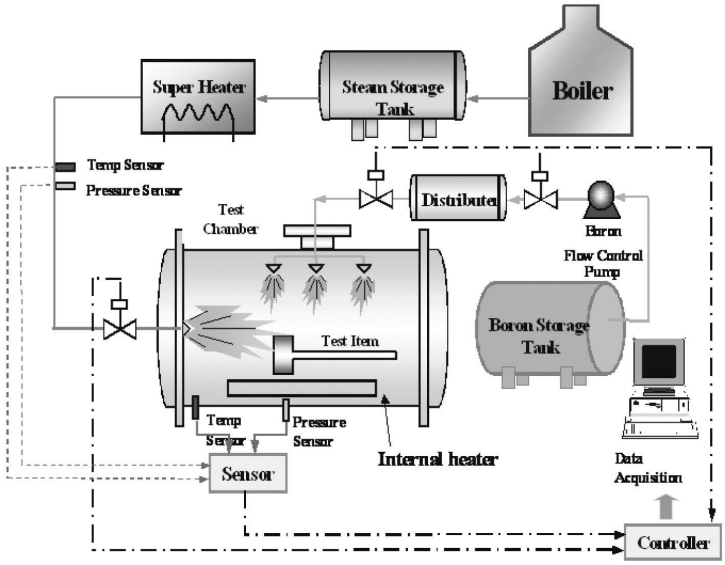


Fig. 3. Schematic of LOCA Test Apparatus

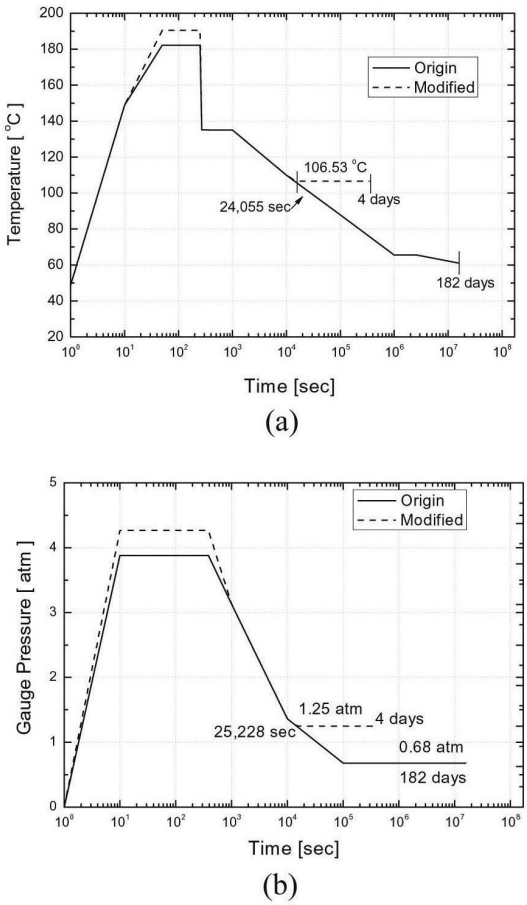


Fig. 4. Original and Modified LOCA T-P Profile at YGN Unit 3&4

3. RESULTS AND DISCUSSION

3.1 Tensile Test

Fig. 5 shows the tensile test results of the elongation at break before and after the LOCA test. As shown in the figure, the elongation at break gradually decreases with an increasing aging temperature, which means that aging steadily takes away its rubber-like large ductility. The figure also shows that the decrease becomes relatively severe at high temperatures above 155ºC compared to that at the temperature of 140ºC On the other hand, it turns out that the LOCA experience does not alter this aging trend as much when the aging temperature goes up above 155ºC.

In the polymer industry, it is believed that the elastomer is no longer serviceable when its elongation at break reaches 50% or 60% of the initial elongation of the intact materials [19]. In this study, for a conservative approach, 60% elongation at break was chosen to be the lifetime of EPDM. According to the definition, the lifetime of EPDM isothermally aged at 140ºC is 1,316 hours, which is then reduced to 1,120 hours after experiencing the LOCA environment. For reference, these estimated lifetimes with standard deviations are tabulated in Table 2.

The activation energy of the elongation reduction was examined using the following Arrhenius model:

$$\ln L = \left[-\left(\frac{E}{kT} \right) \right] + \ln A \qquad (2)$$

where A is the frequency factor, E is the activation energy

Table 2. Life Time and Standard Deviation

TEMP. (°C)	Before LOCA		After LOCA	
	Life time (h)	Standard deviation (h)	Life time (h)	Standard deviation (h)
140	1316	322	1120	265
155	368	81	384	153
170	171	48	189	52

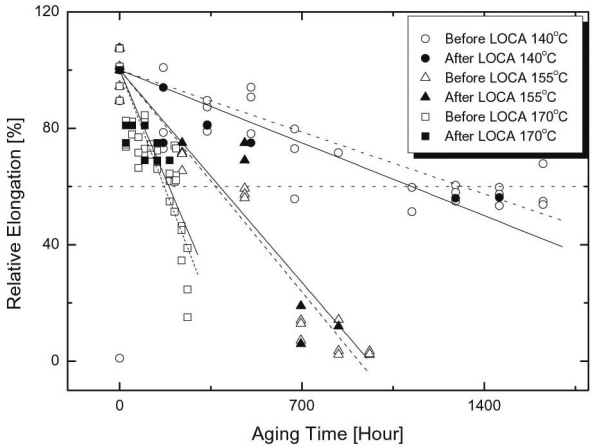


Fig. 5. Relative Elongation Changes with Various Aging Times and Temperatures Before and After LOCA Experience

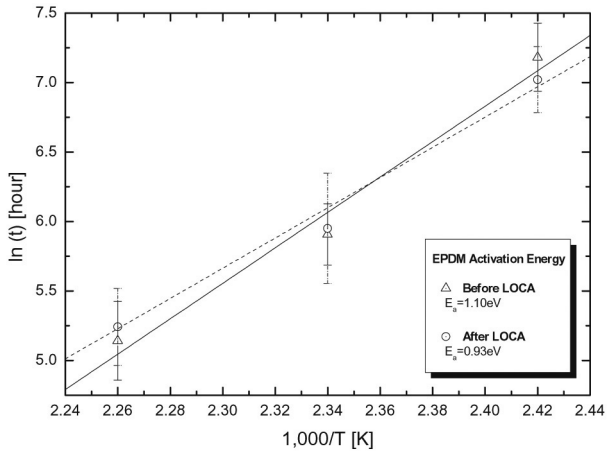


Fig. 6. Activation Energy Changes of Elongation at Break Before and After LOCA Experience

in eV, k is the Boltzmann's constant, T is the absolute temperature in K, and L is the thermal lifetime. The energies were determined to be 1.10 ± 0.196 eV and 0.93 ± 0.191 eV before and after the LOCA condition, respectively (Fig. 6). As mentioned earlier, this activation energy drop is mainly ascribed to the aging enhancement at 140°C

It is generally accepted that the degradation of polymeric materials is principally due to the oxidation of constituent elements [20-21]. The oxygen attack may take place dominantly on the carbons atoms of EPDM where degradation starts on the weakest spots of the macromolecules exposed to the oxygen environment. The reaction with the oxygen atoms/radicals makes the materials brittle, which causes the decrease of ductility or elongation. Lengthy aging at a relatively high temperature may also cause the scissions of the molecule bonds, which leads to the loss of elasticity for EPDM.

In short, it can be inferred that not only the aging of EPDM, but also a severe accident environment such as LOCA, can considerably reduce the mechanical integrity and lifetime of the elastomer. In the meantime, it was also found that the short period accident experience does not significantly influence the aging degradation as its aging temperature becomes higher.

3.2 Thermo-Gravimetric Analysis

The aging decomposition of the EPDM was examined through weight loss measurement using a Thermo-Gravimetric Apparatus (TGA). Current analysis followed the procedure proposed and described in ISO 11358 and ASTM E1641-04 [15]:

$$E = -\frac{R}{b}\left[\frac{d\log\beta}{d(1/T)}\right] \tag{3}$$

where E is the Arrhenius activation energy in J/mol, R is the gas constant, β is the heating rate in K/min, T is the absolute temperature in K, and b is the approximated value for the derivative (b = 0.457/K on first iteration recommended in ASTM1641-04).

Fig. 7 shows that the EPDM rarely decomposes at temperatures below 300°C, but remarkable weight loss

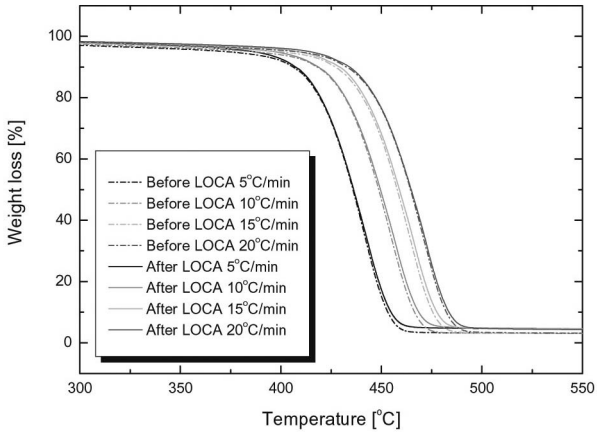


Fig. 7. Thermal Decomposition Curve with Various Heating Rates Before and After LOCA Experience

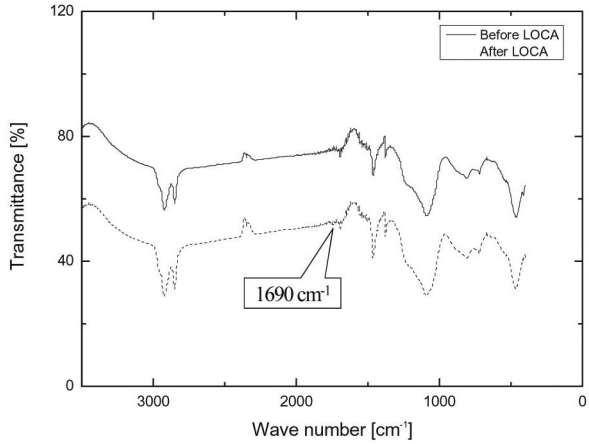


Fig. 9. FT-IR Spectra of EPDM Before and After LOCA Experience

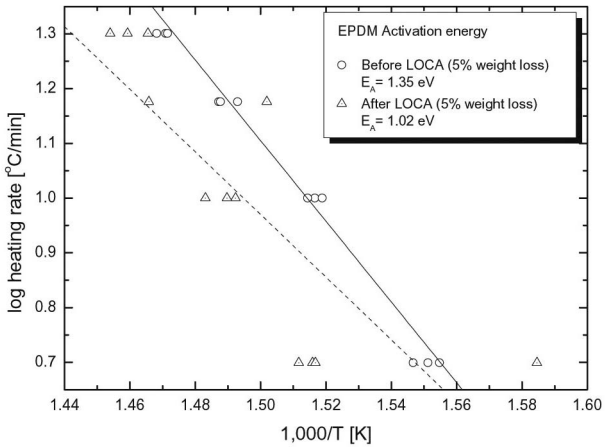


Fig. 8. Activation Energy Changes of Aging Decomposition Before and After LOCA Experience

was observed at temperatures above 400ºC, and it was discovered that as the heating rate decreases, decomposition proceeds very vigorously. The log(heating rate) vs. 1/T plot based on 5% weight loss decomposition is shown in Fig. 8, which reveals the activation energy of the thermal decomposition of the aged EPDM.

The energies were derived to be 1.35 eV and 1.02 eV before and after experiencing the LOCA condition, respectively. These results imply that EPDM may easily degrade with the decomposition once it undergoes very harsh environments, such as the LOCA situation. However, these activation energies do not have to be directly compared to those of the elongation reduction because their degradation mechanisms are different.

Previous studies have [13,22] claimed that the decomposition of EPDM is due to the random chain-scission progressively taking place along the chain until the fragments are small enough to volatilize. They demonstrated that the activation energy seems to be controlled by both the ethylene content and the micro-structural changes.

3.3 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

In order to analyze the carbonyl reactions before and after the LOCA experience, FT-IR (model MAGNa-IR 760, E.S.P Co.) analyses were performed. Comparison of the FT-IR spectra before and after the LOCA test in Fig. 9 reveals no new absorption peaks. It is generally known that when polymeric materials are thermally degraded, particularly at a high temperature and high pressure, polymeric chains begin to respond weakly to oxygen and form free radicals with oxygen (C=O) later. If the reaction products become volatile, their molecular weight decreases and the remaining scission components recombine with carbon (C=C) and stabilize themselves again [23-25]. However, current FT-IR analysis found that the spectroscopic intensities of C=O groups generated inside the aged EPDM are not high enough to be detected, even though mechanical property changes and thermal decomposition were discernibly observed during the aging process both before and after the LOCA condition.

4. CONCLUSIONS

The aging degradation and lifetime assessment of a domestic class 1E EPDM, a popular insulating material for electrical cables in the nuclear power industry, were

studied for equipment qualification verification under the LOCA condition.

Tensile test results reveal that the elongation at the break and the lifetime of the EPDM gradually decrease with increasing aging temperature. Based on the 60% elongation rule, the estimated lifetime of the elastomer isothermally aged at 140ºC is 1,316 hours and the activation energy of the elongation reduction is 1.10 eV ± 0.196. In the meantime, the TGA test results disclose that the activation energy of the aging decomposition is 1.35 eV.

As expected, it turns out that the LOCA experience, in which ambient temperature and pressure abruptly increase, can further influence the deterioration of the EPDM that was already aged. After experiencing the LOCA environment, the lifetime of the EPDM was reduced to 1,120 hours while the activation energy of the elongation reduction decreased to 0.93 ± 0.191 eV. The TGA test results show that the activation energy of aging decomposition also decreased to 1.02 eV.

FT-IR analysis discloses that the spectroscopic intensities of C=O groups generated inside the aged EPDM are not high enough to be detected, even though mechanical property changes and thermal decomposition were discernibly observed during the aging process both before and after the LOCA condition.

Based on these experimental findings, it is confirmed that not only the aging of EPDM, but also the experience of a severe accident environment such as LOCA, can considerably reduce the mechanical and thermal integrity, as well as the lifetime, of the elastomer. On the other hand, it was also found that the short period accident experience did not significantly influence the aging degradation as its aging temperature is higher.

Through this study it can be concluded that the aging degradation of the domestic class 1E EPDM can be tolerable, even in accident conditions, such as LOCA and, therefore, it is a suitable and qualified insulating material for electrical cables in nuclear power plants.

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