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Degradation Behavior of Electric Cable Materials by Heat and Radiation Aging

Shinichi OKAMOTO*, Yoshihiko SHONO*, Tokuhiro OHNISHI*,
Yoshihiro UEDA**, Yasuyuki NOMURA** and Takuo TANAKA**

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Characteristic changes of electric-cable covering materials, deteriorated by heat or radiation aging, have been examined, and the degradation behavior has been studied by chemical analysis. Thermogravimetry of the materials, whose characteristics have been deteriorated remarkably by aging, has indicated the decrease of the temperature that causes a predetermined weight reduction, and infrared spectroscopy has showed the generation of carbonyl groups. Consequently, it has been found that the decrease in molecular weight and oxidation of polymer have much effect on the degradation in physical properties of the materials.

1. Introduction

More than thirty years have passed since the nuclear power plant started its operation in Japan, and lately there is a trend to investigate the degradation level of the cable materials used in the actual plant, and reflect the result on the future cable lifetime design¹⁻³⁾. Under this circumstance, the present paper describes the changes in the volume resistivity, tensile strength, elongation and hardness of electric-cable covering materials by aging under the environments of heat and radiation, and describes results of studies on the degradation behavior by way of such analytical methods as thermogravimetry and microscopic infrared spectroscopy.

2. Procedure of Test

2.1 Specimens

Samples used for the test have been the covering materials which are in practical use for cables in nuclear power plants, and particularly cured and cross-linked materials have been prepared as the specimens. The materials tested are shown in Table 1.

Although these materials usually have a peculiar tint due to such additives as flame retardant or some colorants, the coloring additives have been excluded in

Table 1 Specimens used for test

Symbol	Materials	Use
FR-XLPE	Flame retardant cross-linked polyethylene	Insulation
FR-EPR	Flame retardant ethylene propylene rubber	Insulation
FR-CR	Flame retardant chloroprene rubber	Jacket
NH-XLPE	Flame retardant non-halogen cross-linked polyethylene	Insulation, Jacket

this test so that the chemical analyses might be easier. The pressed sheets of 1-mm thickness have been used as specimens in this test.

2.2 Aging conditions

As the normal operating conditions in the primary containment vessel of a nuclear power plant, environmental temperature of 60 °C and radiation dose rate of 1.5 Gy/h were assumed, and the specimens were aged under heating or irradiating (by gamma rays from ⁶⁰Co) environment, and these conditions were accelerated by 100 times as shown in Table 2. Regarding the temperature acceleration, the temperature which would be the accelerating ratio of 100 times was calculated from the Arrhenius plots between heat aging temperature of a FR-EPR and the time when its elongation would reduce to 50%. The dose rate for irradiation was determined as the normal operating dose rate multiplied by the accelerating

Table 2 Aging conditions

	Heating temp.(°C)	Dose rate (Gy/h)
Heat aging	107	—
Radiation aging	Room temperature	150

* Research Center of Radiation, Research Institute for Advanced Science and Technology.

** Tatsuta Electric Wire & Cable Co., Ltd.

ratio of 100.

2.3 Measurement items and test method

Each specimen was taken out at one of equivalent exposure times (5, 10, 20, 30 and 40 years). The actual aging times are the quotients of the equivalent exposure years divided by 100. The following characteristics of aged specimens were measured:

- 1) Volume resistivity: Measurement was made after one minute under an applied voltage of 500 V D.C.
- 2) Tensile strength and elongation: JIS No. 3 dumbbell-shaped test pieces were prepared, and the tensile strength and the elongation were measured at the room temperature ($23 \pm 2^\circ\text{C}$) and at the test speed of 200 mm/min.
- 3) Hardness: After piling up the sheets to approximately 6 mm in thickness, the hardness was measured with a Shore D hardness tester at the room temperature.

Further, these specimens were analyzed by the following methods:

- 1) Infrared spectroscopy: We cut the sample into a slice with a microtome, and analysis was made along the depth of the specimen by the transmission method, or along the surface of the specimen by the ATR (Attenuated Total Reflection) method by attaching it tightly on a Ge crystal plate.
- 2) Thermogravimetry: Samples of approximately 10 mg were prepared. Nitrogen gas was made to flow at the rate of 300 ml/min, and the temperature was raised from room temperature to 550°C at the speed

of $20^\circ\text{C}/\text{min}$, and weight reduction was measured.

3) Differential scanning calorimetry: Samples of approximately 10 mg were prepared. Nitrogen gas was made to flow at the rate of 100 ml/min and the temperature was raised from room temperature to 150°C at the speed of $5^\circ\text{C}/\text{min}$, and heat of crystalline fusion was measured.

3. Results and Discussions

3.1 Volume resistivity

Changes in the volume resistivities by heat aging and by radiation aging are shown in Figs. 1a and 1b, respectively. In heat aging, the change of only FR-CR was conspicuous, but the resistivity of the other samples were roughly constant. In the radiation aging, the resistivity of NH-XLPE showed increasing tendency until 10 equivalent-year, and thereafter no remarkable change was observed. FR-XLPE and FR-CR showed gentle decreasing tendency of the volume resistivity with increasing exposure time. For FR-EPR, the resistivity was roughly constant.

From the above results we have found that the volume resistivity of FR-CR is affected mainly by heat aging, and that of FR-XLPE is effected by radiation aging. On the other hand, it has been found that both heat aging and radiation aging does not have much effect on the volume resistivity of NH-XLPE and FR-EPR.

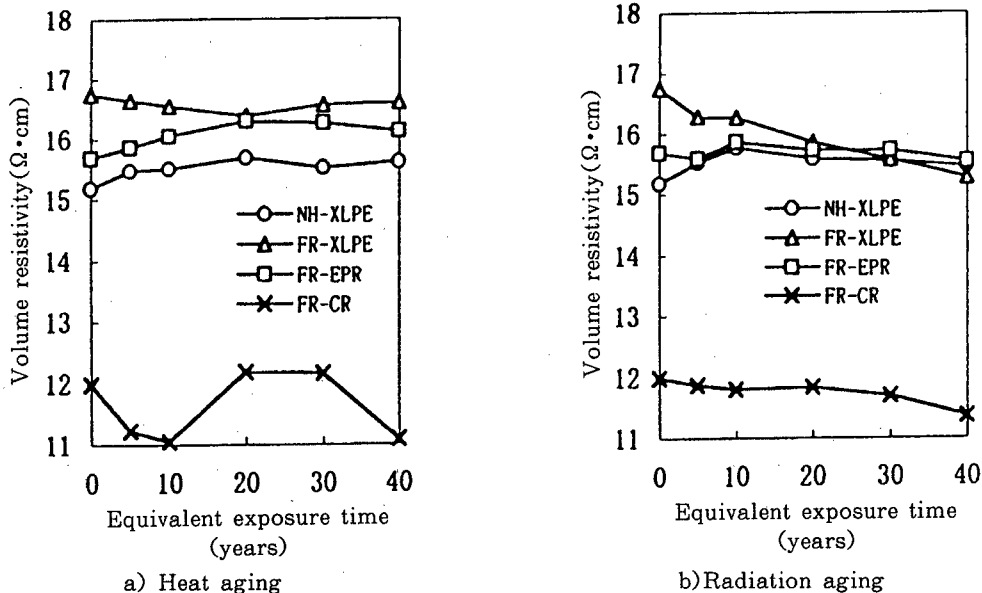


Fig. 1 Relationship between equivalent exposure time and volume resistivity

3.2 Tensile strength and elongation

Changes in the tensile strength by heat aging and radiation aging are shown in Figs. 2a and 2b, respectively. In heat aging, FR-CR showed remarkable changes in tensile strength; it once decreased and then increased greatly. The other materials did not show so much changes. In radiation aging, tensile strength of all materials showed a trend of gradual decrease with increasing exposure time.

Changes in the elongation by heat aging and radiation aging are shown in Figs. 3a and 3b, respectively. In heat aging, FR-XLPE and NH-XLPE did not show appreciable change. FR-EPR showed a trend of slight

decrease with increasing exposure time. On the other hand, FR-CR showed a great decrease, indicating that the lifetime would expire at about 30 equivalent years from the viewpoint of the elongation value, and this fact coincides with the tendency that its tensile strength increased greatly after 30 equivalent years. In radiation aging, elongation of all materials except NH-XLPE decreased remarkably. For FR-CR the decrease of its elongation was more remarkable in heat aging, while for the other materials, the trend of decrease was more notable in radiation aging.

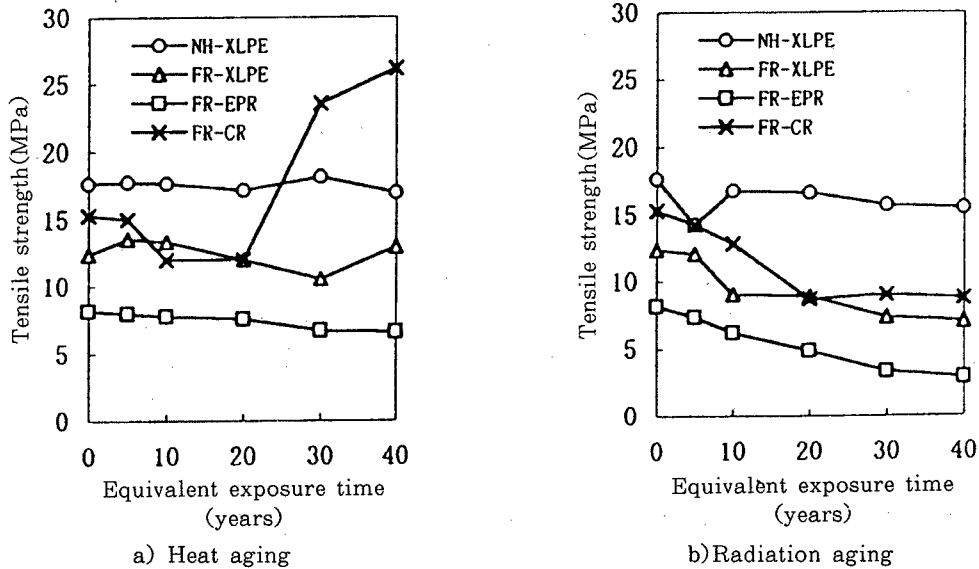


Fig. 2 Relationship between equivalent exposure time and tensile strength

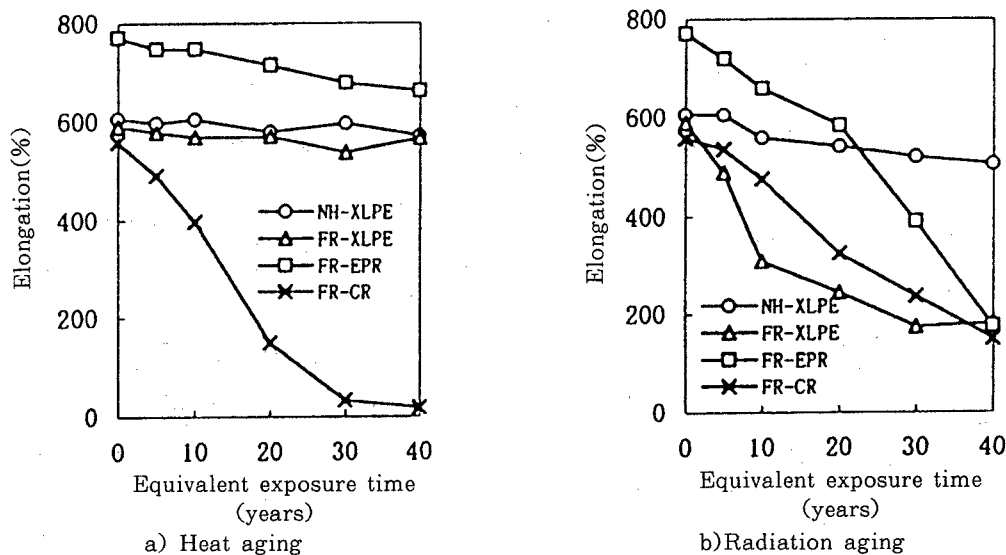


Fig. 3 Relationship between equivalent exposure time and elongation

3.3 Hardness

Changes in the hardness by heat aging and radiation aging are shown in Figs. 4a and 4b, respectively. In heat aging, NH-XLPE and FR-XLPE showed the rise of hardness only at 5 equivalent years, and thereafter no remarkable change was observed. FR-EPR showed little change, while FR-CR showed a great increase of hardness with increasing exposure time. In radiation aging, FR-EPR and FR-CR showed little change in hardness, whereas NH-XLPE and FR-XLPE were seen to show a increase until 5 to 10 equivalent years, and thereafter no remarkable changes were observed.

From the above results, it is considered that FR-XLPE and FR-EPR show a remarkable decrease in elongation by radiation aging, while NH-XLPE, FR-XLPE and FR-EPR does not develop degradation so much by heat aging. Furthermore, for FR-CR degradation proceeds by heat and radiation aging, especially deterioration is great in heat aging.

3.4 Analysis results

3.4.1 Infrared spectroscopy

The infrared spectroscopy analysis for FR-XLPE and NH-XLPE was carried out along the depth of their specimen by the transmission method, and for FR-EPR and FR-CR along the surface of their specimen by the ATR method.

For NH-XLPE, no any change was observed in the spectrum in both heat and radiation aging. For FR-XLPE, the apparent peak of carbonyl group could not be identified in the heat aging. The absorption ratio

of carbonyl group, defined as the absorption ratio of carbonyl-group/methylene-group, at the surface and inner portions along the depth of the specimen, in the radiation aging, is shown in Fig. 5. The specimens, aged for 30 and 40 equivalent years, indicated the peak of carbonyl group. Their absorption ratios were greater near the surface, and were undetectable at the deep inner portion (500 μ m).

For FR-EPR, the apparent peak of carbonyl group could not be identified in heat aging, similar to FR-XLPE. The absorption ratio of carbonyl group, defined again as the absorption ratio of carbonyl-group/methylene-group, is shown in Fig. 6 as a function of exposure time for radiation aging. In this case, the presence of carbonyl group was observed after 20 equivalent years, and the absorption ratio increased with increasing exposure times.

The absorption ratio of carbonyl group, defined in as the absorption ratio of carbonyl-group/silicate ion, at the surface of FR-CR is shown in Fig. 7 as a function of exposure time. The silicate ions were present in a filler added to FR-CR, and were assumed to be stable enough for the reference of the absorption ratio of carbonyl group. The absorption ratio of carbonyl group is seen to increase with increasing exposure time in both heat and radiation aging, but its change is much greater in heat aging than in radiation aging; such difference was not been observed in the other materials. This result coincides with the aforementioned fact that the degradation of FR-CR in volume

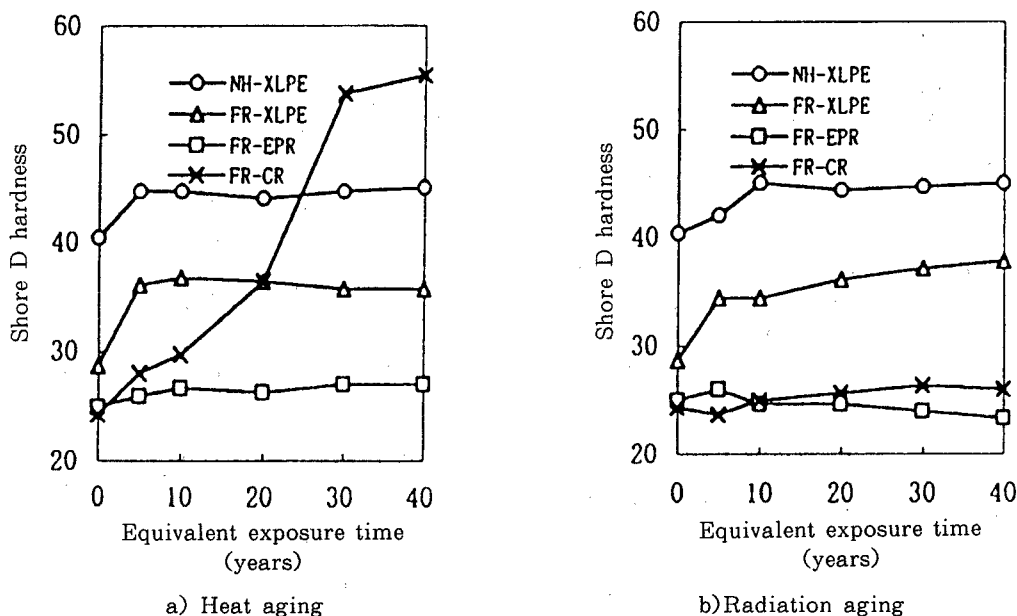


Fig. 4 Relationship between equivalent exposure time and hardness

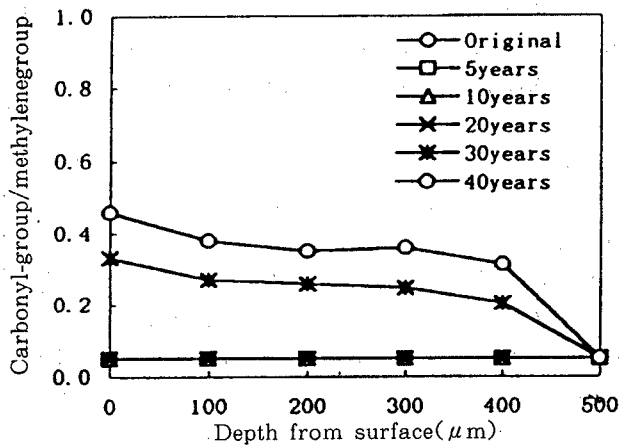


Fig. 5 Change of the absorption ratio of carbonyl-group/methylene-group in the direction of thickness for FR-XLPE with radiation aging.

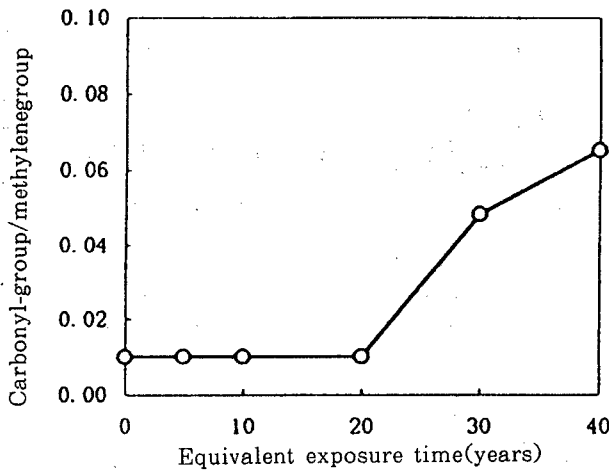


Fig. 6 Relationship between equivalent exposure time and the absorption ratio of carbonyl-group/methylene-group of surface for FR-EPR with radiation aging

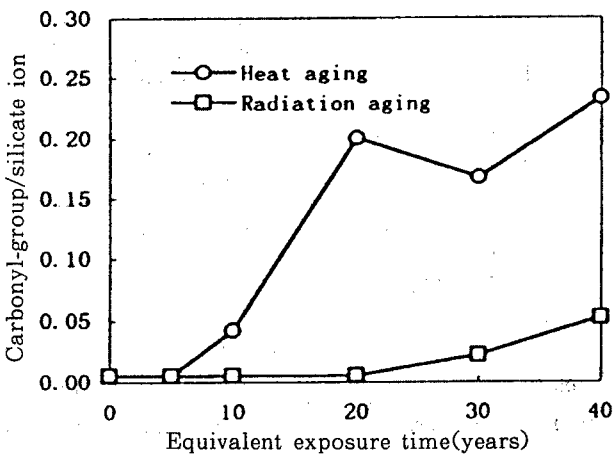


Fig. 7 Relationship between equivalent exposure time and the absorption ratio of carbonyl-group/silicate ion of surface for FR-CR with radiation aging

resistivity and such physical properties as elongation was influenced more by heat aging than by radiation.

From the above results, we have found that the generation of carbonyl group is identified in the materials whose elongation was greatly reduced, and consequently that the oxidation of polymer is one of important causes of the reduction of elongation.

3.4.2 Thermogravimetry

From the measurement of temperature and weight reduction, the temperature at which the weight was reduced by a predetermined amount was read. The relationship between exposure time and the temperature at 5% weight reduction for NH-XLPE is shown in Fig. 8. This temperature showed little change in both heat and radiation aging.

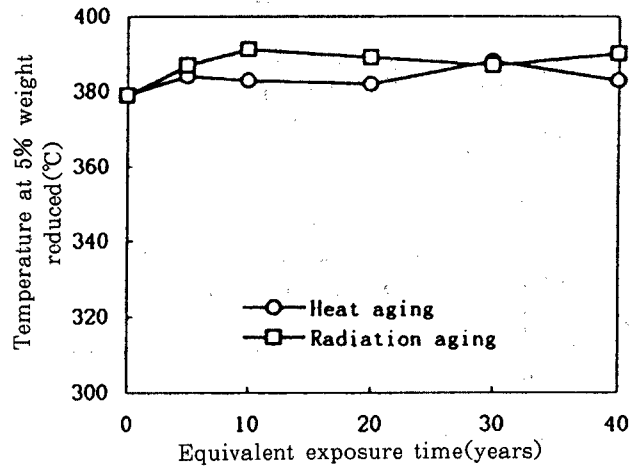


Fig. 8 Relationship between equivalent exposure time and the temperature at 5% weight reduced for NH-XLPE

The relationship between exposure time and the temperature at 25% weight reduction for FR-XLPE is shown in Fig. 9. Although this temperature showed little change in heat aging, it was observed to decrease in radiation aging after 20 equivalent years.

The relationship between exposure time and the temperature at 3% weight reduction for FR-EPR is shown in Fig. 10. Although this temperature showed little change in heat aging, a decrease with increasing exposure time was observed in radiation aging.

The relationship between exposure time and temperature at 5% weight reduction for FR-CR is shown in Fig. 11. In both heat and radiation aging, this temperature decreased remarkably with increasing exposure time. There was no difference between heat and radiation aging in the behavior of this temperature. Thus the decomposition of polymer is considered to be

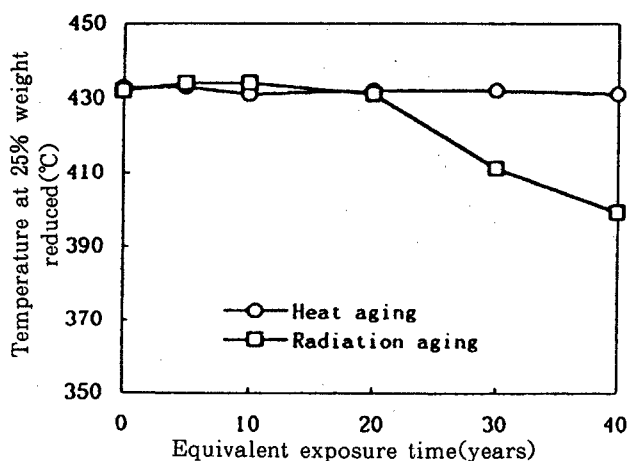


Fig. 9 Relationship between equivalent exposure time and the temperature at 25 % weight reduced for FR-XLPE

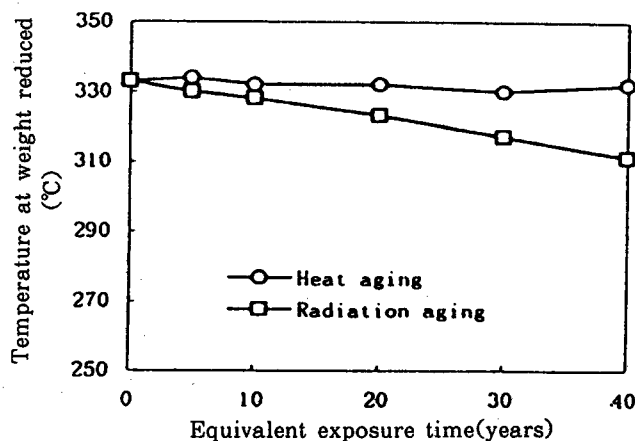


Fig. 10 Relationship between equivalent exposure time and the temperature at 3 % weight reduced for FR-EPR

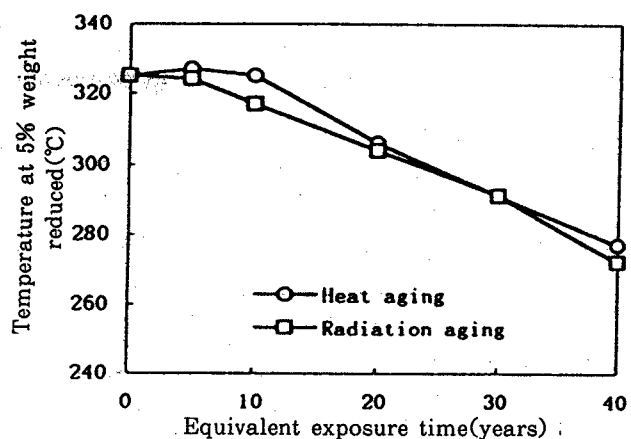


Fig. 11 Relationship between equivalent exposure time and the temperature at 5 % weight reduced for FR-CR

the same level independent of the aging environment, though in the infrared spectroscopy described above, much difference in the generation of carbonyl group

was observed between the aging environments, with higher oxidation of polymer in heat aging.

3.4.3 Differential scanning calorimetry

The relationship between exposure time and heat of crystalline fusion for NH-XLPE is shown in Fig. 12. Little change was observed in both heat and radiation aging. Relationship between exposure time and heat of crystalline fusion for FR-XLPE is shown in Fig. 13. In heat aging, heat of crystalline fusion was roughly constant, but in radiation aging, it increased with increasing exposure time.

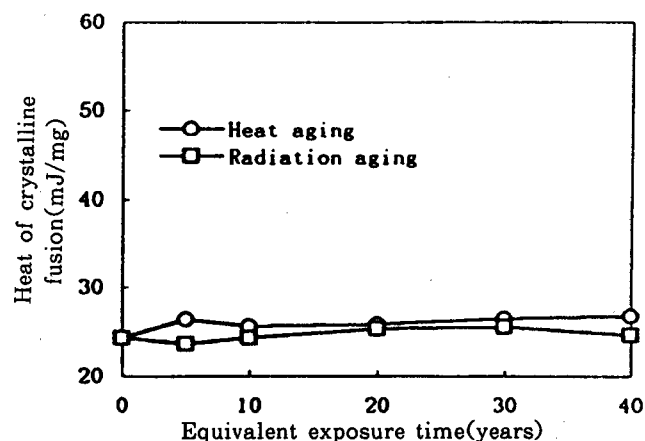


Fig. 12 Relationship between equivalent exposure time and heat of crystalline fusion for NH-XLPE

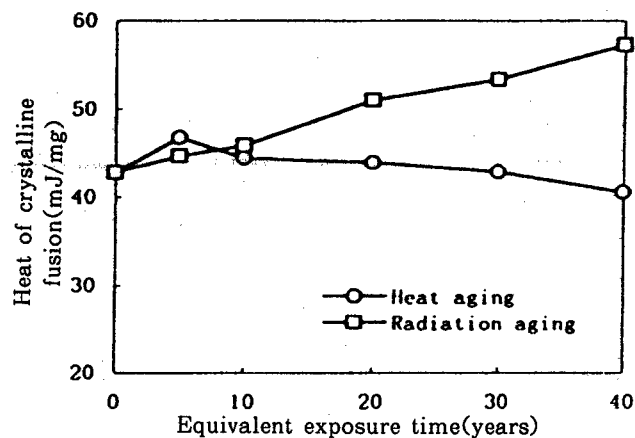


Fig. 13 Relationship between equivalent exposure time and heat of crystalline fusion for FR-XLPE.

Concerning the reason of this result, it can be considered, for example, that the degree of freedom of molecules was increased by the rupture of the molecular chains of the non-crystal portion of polyethylene, thereby part of this portion being crystallized. However, an additional analysis is required to verify this assumption.

4. Conclusion

1) NH-XLPE: The reduction of elongation was small in both heat and radiation aging, and little change was observed in other physical properties. Accordingly, changes were not observed in analytical evaluation either.

2) FR-XLPE and FR-EPR: In heat aging, changes in physical properties were small, and changes were unrecognizable in analytical evaluation. In radiation aging, tensile strength and elongation decreased. Thus it can be considered that there occurred the reduction of molecular weight by oxidation or decomposition of polymer, and the embrittlement by increase of crystallinity.

3) FR-CR: The physical properties were greatly changed, and degradation proceeded. These were caused more remarkably by heat aging than by radiation aging. In the analytical evaluations, no difference in degradation could be seen by thermogravimetry. However, infrared spectroscopy showed that more oxidation was caused by heat aging than by radiation

aging.

Similar degradation behavior of materials that showed notable changes in the physical properties by both heat and radiation aging is considered to be due to the reduction of the molecular weight by oxidation and decomposition of polymer found in all these materials. However, mechanisms other than oxidation and decomposition are considered to be involved in the degradation, because the physical properties of polymer samples with the same level of oxidation showed much differences between heat and radiation aging, as seen in the example of FR-CR.

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