



## Degradation Behavior of Electric Cable Materials by Heat and Radiation (II)

メタデータ	言語: eng 出版者: 公開日: 2010-04-02 キーワード (Ja): キーワード (En): 作成者: Okamoto, Shinichi, Shono, Yoshihiko, Onishi, Tokuhiro, Ueda, Yoshihiro, Nomura, Yasuyuki, Tanaka, Takuo メールアドレス: 所属:
URL	<a href="https://doi.org/10.24729/00008265">https://doi.org/10.24729/00008265</a>

# Degradation Behavior of Electric Cable Materials by Heat and Radiation (II)

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

(Received October 28, 1997)

The characteristic changes and the aging behavior of low density polyethylene and flame retardant low corrosive polyvinyl chloride materials, aged by heat and radiation, have been examined. For polyethylene, it has been verified that the degradation in heat aging is mainly caused by the oxidation of polymers and that the degradation in radiation aging is mainly due to the cross-linking of polymers by gamma rays. For flame retardant low corrosive polyvinyl chloride, it has been found that the degradation in heat aging is mainly caused by the volatilizing of plasticizer, and that the degradation in radiation aging is mainly caused by the changes of polymer structure.

## 1. Introduction

More than 30 years have passed since the nuclear power plant started its operation in Japan, and presently there is a trend to investigate the degradation level of cable materials in the actual field and to reflect the results on the future cable design for longer lifetime. On such a background, the degradation behavior of rubber and crosslinked cable covering materials for the nuclear power plants, aged under the environments of heat and radiation, was studied in the previous paper<sup>1)</sup>. In the materials conspicuously degraded in the physical properties by aging, the drop of the temperature for the predetermined amount of weight reduction was observed by means of thermogravimetry, and the generation of the carbonyl group was observed by means of infrared spectroscopy. From these results, it was found that the degradation of physical properties could be attributed mostly to the reduction of molecular weight and the oxidation of polymers.

In the present work we have examined the changes of physical properties in polyethylene and flame retardant low corrosive polyvinyl chloride materials by aging under heat and radiation. Furthermore, studies of aging behavior have been made by means of such analytical methods as thermogravimetry and

microscopic infrared spectroscopy.

## 2. Experimental

### 2.1 Specimens

In the present test, the pressed sheets of about 1-mm thickness of low density polyethylene (LDPE) and flame retardant low corrosive polyvinyl chloride materials (FR-PVC) were selected as specimens.

### 2.2 Conditions of aging test

The materials selected as specimens in this test are not for the use inside the primary containment vessel (PCV) of nuclear power plants, but for the use under more mild environment outside the PCV. For the acceleration of aging, however, tests were conducted under the accelerated conditions of environment inside of PCV. The acceleration conditions were determined on the assumption that the normal operating conditions are the ambient temperature of 60°C and the radiation dose rate of 1.5 Gy/h. The specimens were aged under heating or irradiating (gamma rays from <sup>60</sup>Co) environment, whose conditions were accelerated by 100 times as shown in Table 1. Regarding the temperature acceleration, the temperature corresponding to the accelerating ratio of 100 was calculated from the Arrhenius plots between heat aging temperature of flame retardant EP-rubber (FR-EPR) and the aging time for the reduction of its elongation to 50%. Regarding the radiation, the specimens were irradiated under the dose

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

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

Table 1 Aging conditions

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

rate obtained by the multiplication of the normal operating dose rate by 100.

### 2.3 Measurement items

The specimens were taken out at the equivalent exposure time of 5, 10, 20, 30, 40 and 60 years according to the respective conditions (the actual aging times are the quotients of the equivalent exposure year divided by 100), and the following characteristics were measured.

I) Volume resistivity : Measurement was made after one minute under an applied voltage of D.C.500 V .

II) Tensile strength and elongation: JIS No.3 dumbbell-shaped test pieces were prepared, and tensile strength and elongation were measured at room temperature ( $23 \pm 2$  °C) and at the test speed of 200 mm/min.

III) Hardness : After piling up the sheets to approximately 6 mm in thickness, hardness was measured with a Shore D hardness tester at room temperature.

IV) Thermal stability test: The time until the Congo-red test paper showed color change was measured according to JIS K 6723. The measuring temperature was 190°C.

The specimens were aged under the conditions described above, and analyzed for the items below.

I) Infrared spectroscopy: The specimens were sliced with a microtome, and the infrared spectroscopy was conducted along the depth of the specimen by the transmission method.

II) Thermogravimetry : The samples of approximately 10 mg were prepared. Nitrogen gas was flowed at the rate of 300 ml/min, and the temperature was raised from room temperature to 550 °C at the speed of 20 °C/min, and weight reduction was measured.

III) Gel fraction: After extracting from about 0.3 g of the sheet specimen in a solvent for 24 hours, the gel component was picked out, dried and weighed. Gel fraction was calculated from the weight by the following equation.

$$X = m_2/m_1 \times 100,$$

where X is gel fraction,  $m_1$  is the mass before extracting; and  $m_2$  is the mass after drying. The extracting solvents and the extracting temperatures are shown in Table 2.

Table 2 Extraction condition

	Solvent	Extracting temperature(°C)
LDPE	Xylene	120
FR-PVC	Tetrahydrofuran(THF)	35

The following test items were added to the analysis of FR-PVC.

IV) Gel permeation chromatography: After the specimen of about 40 mg was dissolved in 10 ml of THF, the solution was separated by a centrifugal separator. The component dissolved in THF was analyzed by gel permeation chromatography.

V) Gas chromatography: After the specimen of about 300 mg was extracted in 10 ml of THF, methanol was added to the solution to separate the polyvinyl chloride component. The plasticizer contained in the residual solution was analyzed quantitatively by gas chromatography.

## 3. Results and Discussions

### 3.1 Volume resistivity

The changes in volume resistivity by heat and radiation aging are shown in Figs. 1a) and 1b), respectively. In heat aging, the volume resistivity of LDPE decreased greatly with increasing exposure time, while that of FR-PVC showed a tendency of increasing once and then decreasing. In radiation aging, on the other hand, the volume resistivity of LDPE showed a remarkable drop at the 5 equivalent exposure years, and thereafter became almost constant. FR-PVC showed little change.

The above results indicate that the volume resistivity of LDPE is affected mainly by radiation, and that of FR-PVC by heat.

### 3.2 Tensile strength and elongation

The changes in tensile strength by heat and radiation aging are shown in Figs. 2a) and 2b), respectively. In heat aging, the tensile strength of LDPE showed a drop once at 5 equivalent exposure year and became roughly constant after that. The tensile strength of FR-PVC showed little change. In radiation

aging, on the other hand, the tensile strength of both the materials showed a trend of decreasing with increasing exposure time.

The changes in elongation by heat and radiation aging are shown in Figs. 3a) and 3b), respectively. In heat aging, LDPE showed a large drop of elongation at 20 equivalent exposure years. FR-PVC showed a trend of a slight decrease with increasing exposure time. In radiation aging, on the other hand, both the materials showed a tendency of decreasing with increasing exposure time, until they came to the end of life at 40 equivalent exposure years, when the elongation reaches approximately 50%.

### 3.3 Hardness

The changes in hardness by heat and radiation aging are shown in Figs. 4a) and 4b), respectively. In heat aging, LDPE showed an increase of hardness until 10 equivalent exposure years, and thereafter a slow decrease. FR-PVC showed a tendency of a large increase with increasing exposure time. In radiation aging, on the other hand, both the materials showed a trend of a slow increase with increasing exposure time.

### 3.4 Thermal stability

The thermal stability of FR-PVC is shown in Fig. 5. The time, during which the stability was kept, decreased with increasing exposure time. The time under radiation aging showed a tendency of being slightly lower than that under heat aging.

The correlation between the stability and the elongation is shown in Fig. 6.

This figure shows that the elongation decreases together with the stability independently of the aging condition.

### 3.5 Results of analysis

#### 3.5.1 Infrared spectroscopy

The infrared spectroscopy was made along the depth of the specimen by the transmission method. The distributions of carbonyl groups in LDPE [ peak intensity ratio:  $C=O(1716\text{ cm}^{-1})/CH_2(1464\text{ cm}^{-1})$  ] under heat aging and radiation aging are shown in Figs. 7a) and 7b), respectively. In heat aging, the generation of the carbonyl group was kept under the detectable limit until 10 equivalent exposure years, while, from 20 equivalent exposure years, the carbonyl group became detectable and thereafter advanced to larger depths. At 20 equivalent exposure

years, the peak intensity ratio was relatively higher near the surface and had a tendency of decreasing toward larger depths. On the contrary, the peak intensity ratios in the period from 30 to 60 equivalent exposure years showed roughly the same level at the surface and the inside. Particularly, the concentrations of carbonyl group are considered to have been saturated, from observation that there was but a small difference between 40 and 60 equivalent exposure years. The generation of the carbonyl group was observed at and after 20 equivalent exposure years, and it coincided with the observation that the elongation showed a large drop at 20 equivalent exposure years as described in section 3.2.

In radiation aging, on the other hand, the peak of the carbonyl group showed sharp rise with increasing exposure time, but these ratios as a function of depth showed a rapid decrease with increasing depth. This is possibly caused by the fact that oxygen diffuses more slowly than the degradation progresses due to the relatively low test temperature.

For FR-PVC, the hydrogen chloride, generated by dehydro-chlorination of polymer, is considered to react with the calcium carbonate added as a filler, resulting a highly hygroscopic calcium chloride. Therefore, the concentration of the hydroxyl group, which might have been generated by the absorption of moisture in air, was examined along the depth direction.

In Fig. 8, the distribution of hydroxyl groups [ peak intensity ratio:  $OH(3421\text{ cm}^{-1})/CaCO_3(874\text{ cm}^{-1})$  ] in FR-PVC under radiation aging is shown. In heat aging, the peak of the hydroxyl group could not be detected. In the figure, hydroxyl group is seen at and after 30 equivalent exposure years, and its peak intensity has a tendency to increase with increasing exposure time. Concerning the dependence on depth, at 60 equivalent exposure years the generation of the hydroxyl group was observed much more around the surface of specimen, while at 30 and 40 equivalent exposure years the distributions of hydroxyl groups were nearly uniform except the largest depth.

Because FR-PVC contains the carbonyl group also in the plasticizer, it is impossible to analyze only the carbonyl group contained in the PVC resin from FR-PVC itself. Accordingly, prior to infrared spectroscopy, the specimen was dissolved in THF, and polymer was picked up with a centrifugal separator

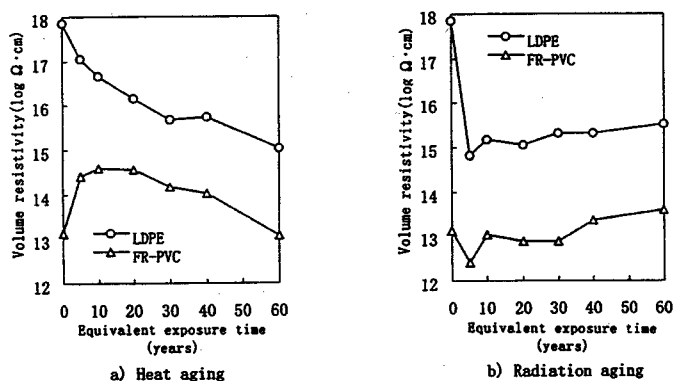


Fig. 1 Relationship between equivalent exposure time and volume resistivity; (a) heat aging and (b) radiation aging

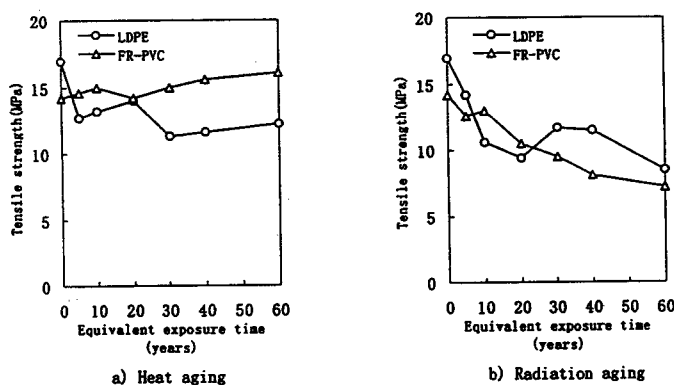


Fig. 2 Relationship between equivalent exposure time and tensile strength; (a) heat aging and (b) radiation aging

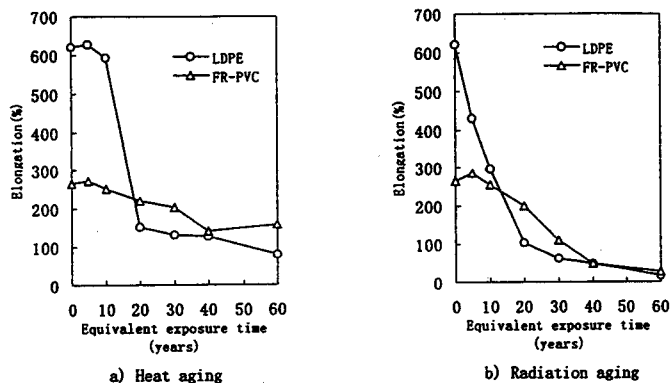


Fig. 3 Relationship between equivalent exposure time and elongation; (a) heat aging and (b) radiation aging

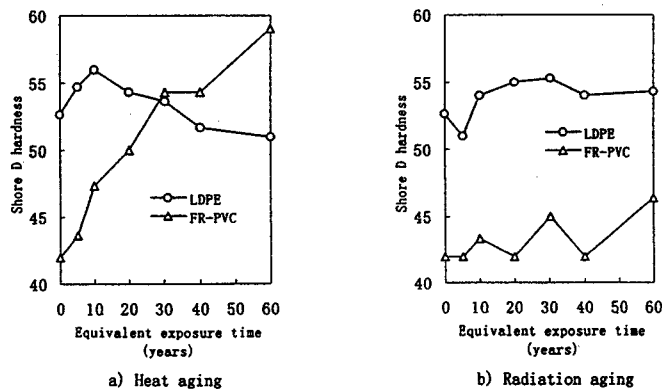


Fig. 4 Relationship between equivalent exposure time and hardness; (a) heat aging and (b) radiation aging

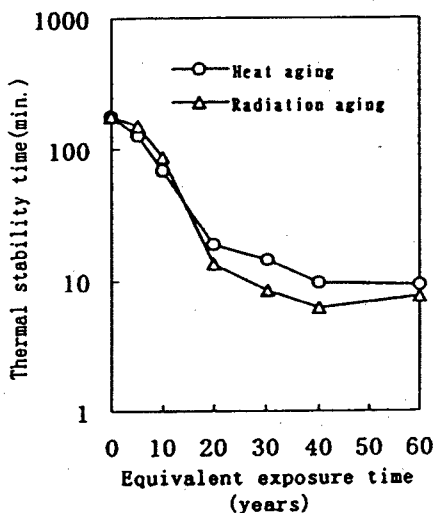


Fig. 5 Relationship between equivalent exposure time and thermal stability time for FR-PVC.

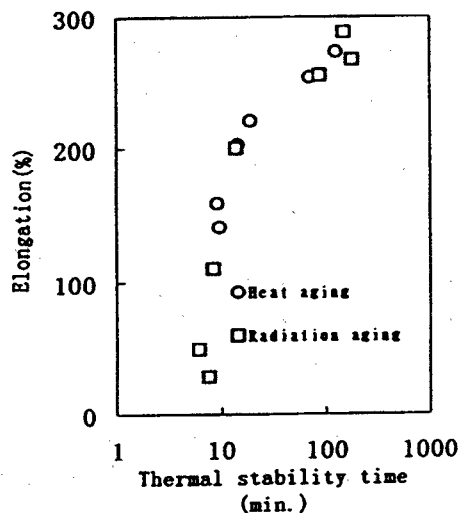
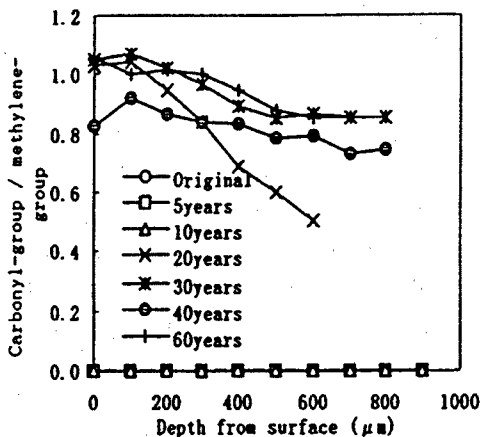
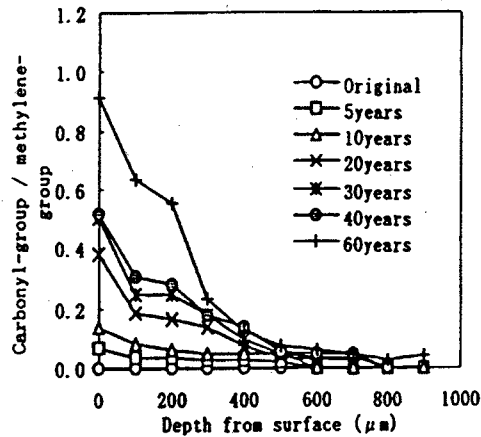


Fig. 6 Relationship between thermal stability time and elongation for FR-PVC.



a) Heat aging



b) Radiation aging

Fig. 7 Changes of the absorption ratio of carbonyl-group/methylene-group in the direction of thickness for LDPE with heat aging and radiation aging

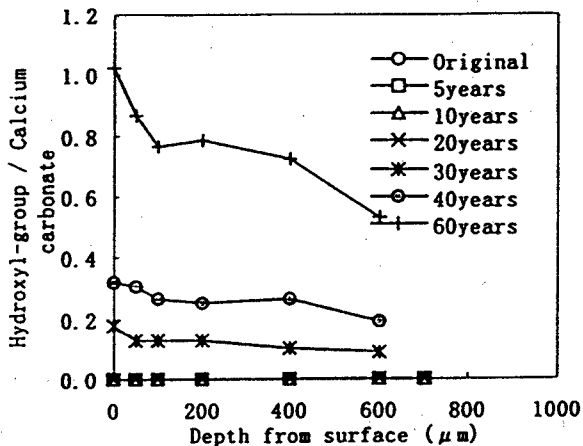


Fig. 8 Change of the absorption ratio of hydroxyl-group/calcium carbonate in the direction of thickness for FR-PVC with radiation aging

from THF solution by precipitating with the mixed solution of methanol and chloroform. Then, the polymer was analyzed by infrared spectroscopy to determine the peak intensity ratio of the carbonyl group ( $1725\text{ cm}^{-1}$ ) vs. PVC ( $1334\text{ cm}^{-1}$ ), and thereby the degree of oxidation in PVC resin was estimated. The result is shown in Fig. 9. The generation of the carbonyl group in heat aging could be observed but at a lower level. In radiation aging, on the contrary, the peak of the carbonyl group showed a conspicuous increase with increasing exposure time.

As described above, it has been found that, in the case of LDPE, heat aging results in oxidation that reaches large depths, and the radiation aging results in oxidation near the surface of the specimen, though the elongation at and after 30 equivalent exposure years becomes less than about 100% independently of the aging condition. In the case of FR-PVC, on the other hand, it has been found that heat aging results in only a low degree of oxidation of PVC resin as indicated by undetectability of dehydrochlorination and that radiation aging results in active reactions of dehydrochlorination and oxidation.

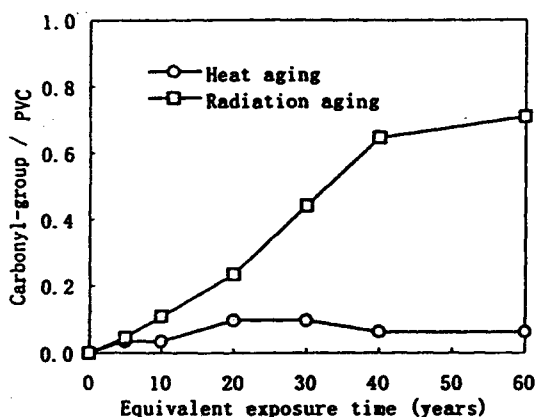


Fig. 9 Relationship between equivalent exposure time and the absorption ratio of carbonyl-group/PVC of surface for FR-PVC with heat aging and radiation aging.

### 3. 5. 2 Thermogravimetry

From the measurement of temperature and weight reduction, the temperature for 5% weight reduction was determined. The relationship between the temperature for 5% weight reduction and the equivalent exposure time is shown for LDPE in Fig. 10. In heat aging, the temperature for 5% weight reduction

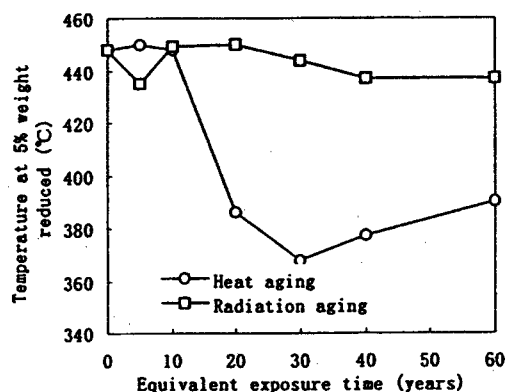


Fig. 10 Relationship between equivalent exposure time and temperature at 5% weight reduced for LDPE.

showed a large decrease at and after 20 equivalent exposure years, while, in radiation aging there was but little changes. From these results, it is inferred that in heat aging the decomposition temperature was lowered by the decrease of molecular weight, while, in radiation aging, both cross-linking and decomposition occurred simultaneously so that the decomposition temperature did not show apparent changes. The relationship between the temperature for 5% weight reduction and the equivalent exposure time is shown for FR-PVC in Fig. 11. In heat aging the decomposition temperature showed little changes, while in radiation aging it decreased with increasing exposure time. These results indicate that molecular weight of LDPE is decreased by heat aging, while that of FR-PVC is decreased by radiation aging.

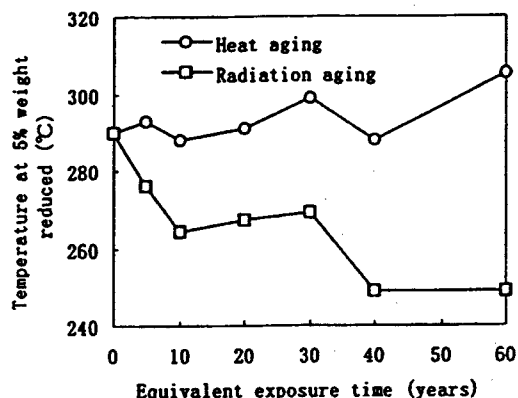


Fig. 11 Relationship between equivalent exposure time and temperature at 5% weight reduced for FR-PVC

### 3. 5. 3 Gel fraction

The changes in the gel fraction under heat and radiation aging are shown in Figs. 12a) and 12b),

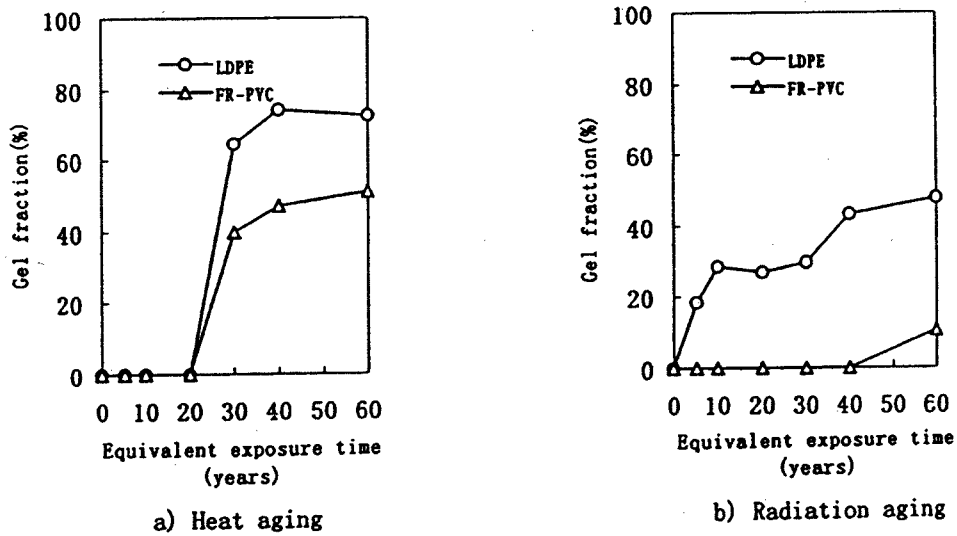


Fig. 12 Relationship between equivalent exposure time and gel fraction

respectively. In heat aging, both the materials showed the same tendency that the gel fraction was increased at 30 equivalent exposure years and thereafter. In radiation aging, the gel fraction of LDPE increased with increasing exposure time, while that of FR-PVC increased only slightly at 60 equivalent exposure years. In the case of LDPE, gelling could be observed in both of the aging conditions, but particularly, the gelling before 20 equivalent exposure years was conspicuous only in radiation aging. This result suggests that in the radiation aging of LDPE, cross-linking by gamma-rays is dominant. The two analyses described below were conducted only for FR-PVC.

### 3. 5. 4 Gel permeation chromatography

The polystyrene-equivalent mean molecular weight, which was obtained by the gel permeation chromatography of FR-PVC dissolved in the THF solution, is plotted in Fig. 13. In heat aging, appreciable changes of the molecular weight as a function of exposure time were not observed. In radiation aging, on the other hand, the molecular weight decreased with increasing exposure time. This reduction of the molecular weight is considered due to the scission of molecular chains by gamma rays. The dehydrochlorination of PVC resin results in the generation of polyene. In connection with this, the gas chromatography of the THF solution was conducted to verify whether the double bond components such as polyene are produced by the degradation of FR-PVC. The result is shown in Fig. 14. The peak area ratio increased with increasing exposure time under both

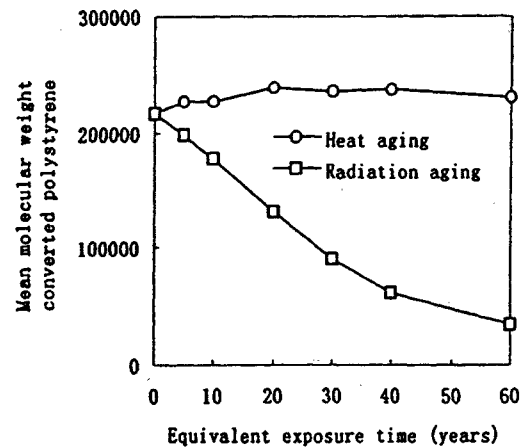


Fig. 13 Relationship between equivalent exposure time and mean molecular weight for FR-PVC.

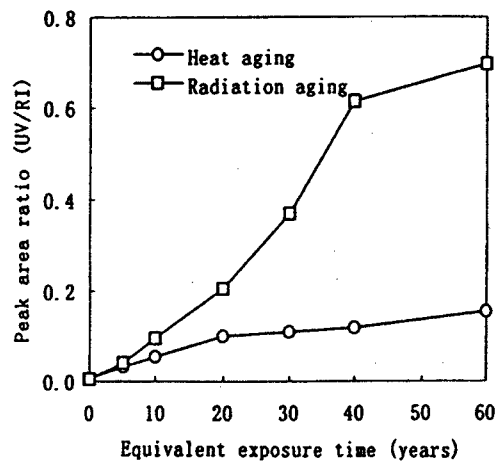


Fig. 14 Relationship between equivalent exposure time and peak area ratio for FR-PVC.



of the aging conditions, and the degree of the change was larger in radiation aging. This result indicates that the dehydrochlorination is more conspicuous in radiation aging than in heat aging. Moreover, when polyene is generated by dehydrochlorination, FR-PVC changes its color into brown. To say more precisely, FR-PVC changes its color when the polyene structure has longer chains, but it does not change color when the polyene has shorter chains. It is considered from the observation of specimen's color that in heat aging the extent of color change is larger due to the generation of the species of polyene having longer chains and that in radiation aging it is smaller due to the species of polyene with shorter chains.

### 3. 5. 5 Gas chromatography

The quantitative analysis of plasticizer was conducted by gas chromatography to determine the residual ratio of plasticizer under degradation. The relationship between the residual ratio of plasticizer and the equivalent exposure time is shown in Fig. 15. In both of the aging conditions, a tendency was observed that the plasticizer residual ratio decreased with increasing exposure time. It is known that the degradation of flexible PVC is mainly caused by the volatilizing and diffusion of plasticizer. Accordingly, in heat aging, the volatilizing due to heat are considered to be dominant. In radiation aging, however, the reduction of plasticizer is larger than in heat aging, in spite of the test condition of irradiation at room temperature. It may be attributed to the reduction of

plasticizer retention capacity of PVC resin itself, which would be caused by the serious degradation of PVC resin due to the action of gamma rays.

## 4. Conclusion

The degradation behaviors of LDPE and FR-PVC under aging conditions of heat and radiation are summarized below.

1) LDPE: In heat aging, it is considered that the degradation due to the decrease of molecular weight and oxidation is dominant, from the observation of the generation of the carbonyl group reaching large depths. In radiation aging, on the other hand, it is considered that the degradation due to the cross-linking by the action of gamma rays is dominant, from the observation that the generation of the carbonyl group occurred only near the surface but to a degree less than that under heat aging.

2) FR-PVC: In heat aging, the degradation is considered to be mainly caused by the volatilizing of plasticizer, from the observation that dehydrochlorination and the generation of the carbonyl group occurred to a small degree. In radiation aging, on the other hand, not only the occurrences of dehydrochlorination and the generation of the carbonyl group but also the decrease of molecular weight was found, and consequently, it can be inferred that the degradation is mainly caused by the changes of such polymer structure.

## Reference

- 1) S. Okamoto, Y. Shono, T. Ohnishi, Y. Nomura, Y. Ueda, and T. Tanaka, *Bull. Osaka Prefect. Univ. A*, **46**, 17 (1997).

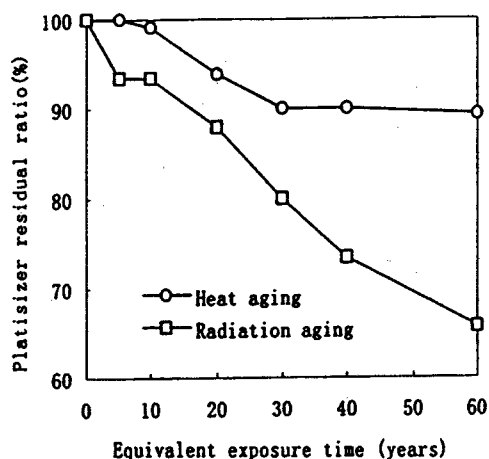


Fig. 15 Relationship between equivalent exposure time and plasticizer residual ratio for FR-PVC.