Chemical Property Change of Cable Jacketing PVC under Heat-Radiation Exposure

Bulletin of University of Osaka Prefecture
Vol. 44, No. 1, 1995, pp. 33-36

Chemical Property Change of Cable Jacketing PVC under Heat-Radiation Exposure

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(Received June 30, 1995)

We studied property change of polymer, plasticizer, and filler contained in polyvinyl chloride (PVC) used as cable jacketing materials caused by heat-radiation simultaneous degradation and radiation degradation, respectively. Remarkable changes in gel ratio and plasticizer residual ratio were found depending on aging conditions and its period.

1. Introduction

We had made a research on characteristic change in connection with our study about the degradation diagnostic method for low voltage cables used in nuclear power plants by exposing cables to combined heat and radiation with the effective acceleration ratios of 100, 300, and 1,000[1,2]. As a result of this research, we already reported the possibility of performing cable degradation diagnosis from the measured values of cable jacket hardness, cable bending load, and cable torsional torque, all obtained by non-destructive test. The present paper describes the result of our continued research on gamma-ray exposed aging and combined heat-radiation aging of 600-V cables (FR-CV) composed of flame retardant crosslinked polyethylene as insulating material and flame retardant polyvinyl chloride as jacketing material. These cables are used outside of the primary containment vessel (PCV). In the present work attention was given to the cable jacketing materials closely related to cable hardness, and the chemical changes of these materials were investigated.

2. Experiment

2.1 Sample and aging condition

We aged the FR-CV cable of 3×5.5 mm² (thickness of jacket, 1.5 mm; finished outside diameter, 14.5 mmϕ) under the conditions described in Table 1, and then used the jacketing material of this cable as samples. The aging condition of Table 1 was established by setting the normal operating temperature at 60°C and irradiation dose rate at 1.5 Gy/h (total dose of 0.5 MGy/40 years). Gamma rays with ^{60}Co source were used as ionizing radiation in the present work. The effective acceleration ratio was made 1,000. As for temperature, we first obtained the activation energy from the heat deterioration characteristics of ethylene-propylene-rubber used as insulation for the cable inside PCV, and then calculated the heating temperature equivalent to the effective acceleration ratio of 1,000 at 60°C. Irradiation dose rate was obtained from the dose rate of the actual usage by multiplying it by 1,000. Testing period is shown in Table 2.

2.2 Measured items

PVC compound mainly consists of polyvinyl chloride resin, plasticizer and filler. Therefore, we made the following measurements to study the chemical changes of these components by degradation caused by aging.

(1) Gel ratio measurement

We took a sample of mass 0.2-0.3 g from the jacket-

Table 1 Aging conditions

Condition	Temperature (°C)	Dose rate (Gy/h)
A	Room temperature	1,500
B	130	1,500

Table 2 Aging test period

Equivalent exposure time (years)	10	20	30	40	60
Aging time (years)	83	167	250	333	500

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ing material of the cable, then put it in a test tube. Solvent of tetrahydrofuran (THF) was added, and extraction was made at 35°C for 24 hours. Then gel was taken out and dried in vacuum at 35°C for 24 hours. Gel ratio was calculated by the following expression.

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

X : Gel ratio (%)

m_1 : Sample weight before immersing (g)

m_2 : Sample weight after immersing and vacuum drying (g)

(2) Plasticizer residual ratio measurement

After the sample being extracted with THF, we added methanol to the obtained extract. Then, we quantitatively measured plasticizer contained in vinyl chloride polymer liquid separated by gas chromatography and calculated the residual ratio.

(3) Thermogravimetric analysis

We first weighed the sample of approximately 5 mg with a scale. Nitrogen gas was flowed at the rate of 300 ml/min into a thermogravimeter and the temperature was raised at the speed of 20°C/min., and the weight reduction ratio was measured.

(4) Micro FT-IR analysis

We cut the sample into a slice by using a microtome, and then moved spot (spot size: 50×250μm) from the surface of the cable jacket to the inside by using a micro FT-IR (JEOL IR-MAU124) for analysis.

3. Results and Discussion

Figure 1 shows the change in the gel ratio of the jacketing material exposed to gamma-ray accelerated aging (condition A) and combined heat-radiation accelerated aging (condition B). By this treatment, it has been found that the gel ratio is higher for the combined heat-radiation aging than the gamma-ray aging. In both the aging conditions, the gel ratio becomes higher with increasing exposure time, but after the equivalent exposure time of 30 years, the gel ratio reaches its saturation, and shows no appreciable change thereafter. In general, the gel ratio is said to indicate the degree of cross linking. It is also said that cross linking and decomposition will be simultaneously caused in polymers by irradiation, but that more cross linking reaction will be caused in PVC[3]. Figure 1 shows that cross linking reaction is more accelerated heat-radiation aging than in gamma-ray aging.

Figure 2 shows the change in the plasticizer residual ratio of the cable jacket. The plasticizer residual ratio decreases with increasing exposure time. The amount of decrease is larger for the combined heat-radiation aging than for the gamma-ray aging. When PVC compound is heated, plasticizer will be volatilized and reduced, but it has now been found that it is also

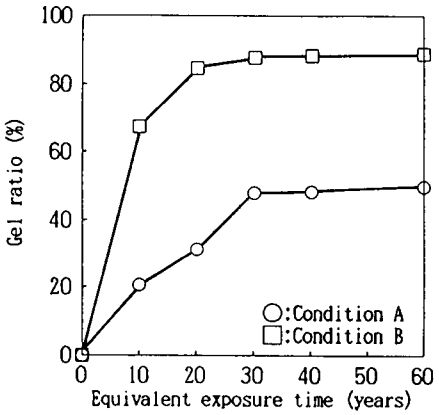

Fig. 1 Relationship between equivalent exposure time and gel ratio.

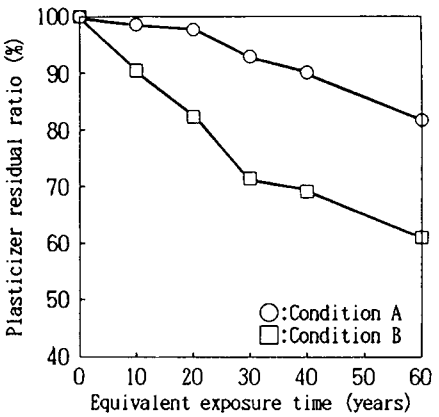

Fig. 2 Relationship between equivalent exposure time and plasticizer residual ratio.

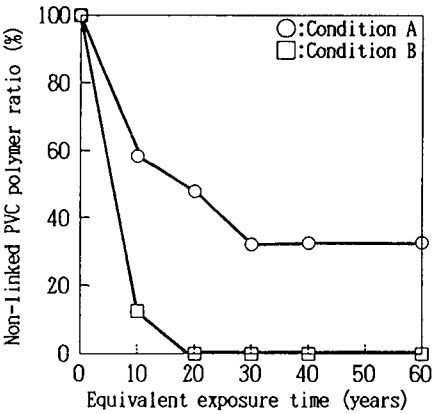

Fig. 3 Relationship between equivalent exposure time and non-linked PVC polymer ratio.

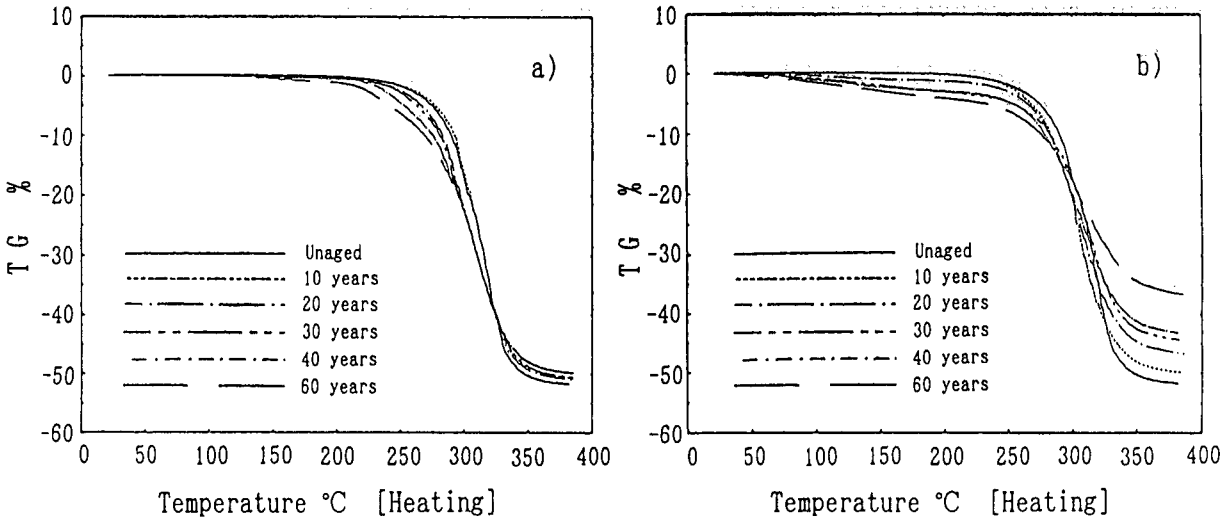

Fig. 4 Weight loss of test samples before and after aging with thermogravimetric analysis.
a) Radiation aging
b) Combined heat-radiation aging

reduced by gamma-ray irradiation at room temperature. The sol component (one minus gel ratio) in Fig. 1 is mainly non-linked PVC polymer and plasticizer. The non-linked PVC polymer ratio was obtained by subtracting the volume of plasticizer obtained in Fig. 2 from the sol component in Fig. 1. This result is shown in Fig. 3. From the result, it can be seen that PVC polymer is almost all cross-linked after the equivalent exposure time of 20 years in the combined heat-radiation aging, but that quite a number of non-linked PVC polymer also remains in the only gamma-ray aging.

The result of the thermogravimetric analysis for the cable jacket is shown in Figs. 4a) and 4b). Figure 4b) indicates that the weight loss is smaller for longer equivalent exposure time at temperatures above 350°C in the case of the combined heat-radiation aging. On the other hand, as shown in Fig. 4a), no remarkable difference in the weight losses of different equivalent exposure times is seen in the case of the gamma-ray aging at temperatures above 350°C. The reason is considered to be in the fact that the temperature at which the molecular chain is cut off is changed due to the difference in the remaining volume of plasticizer for each sample and the difference in degree of cross linking. The temperature of 5% weight reduction determined from Fig. 4 is plotted in Fig. 5. Almost no difference can be seen in 5 % weight reduction temperature between the two aging conditions.

We also studied the property change of calcium carbonate used in filler from micro FT-IR charts. Calcium carbonate captures HCl released from PVC

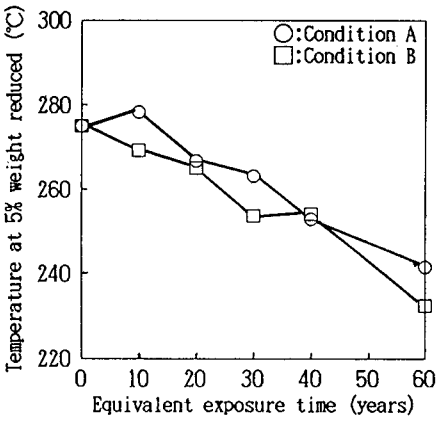

Fig. 5 Relationship between equivalent exposure time and temperature of 5% weight reduction.

and forms calcium chloride. Because calcium chloride has strong hygroscopicity and absorbs moisture, the peak of hydroxyl group (-OH) is detected. Utilizing this nature, we checked the intensity ratio of the absorbance of hydroxyl group at 3410-3440 cm^{-1} against the absorbance of calcium carbonate at 875.53 cm^{-1} at different depths of samples. Figure 6 shows the ratio as a function of depth: a) for radiation aging and b) for the combined heat-radiation aging. In both the aging conditions, the property change of calcium carbonate at the cable surface is large, and becomes much larger with increasing equivalent exposure time. Hydroxyl group peak did not appear and virtually no change in property was noted for the equivalent exposure times of 10, 20, and 30 years in the radiation aging and for the equivalent exposure time of 10 years in the combined heat-radiation aging. For the equivalent

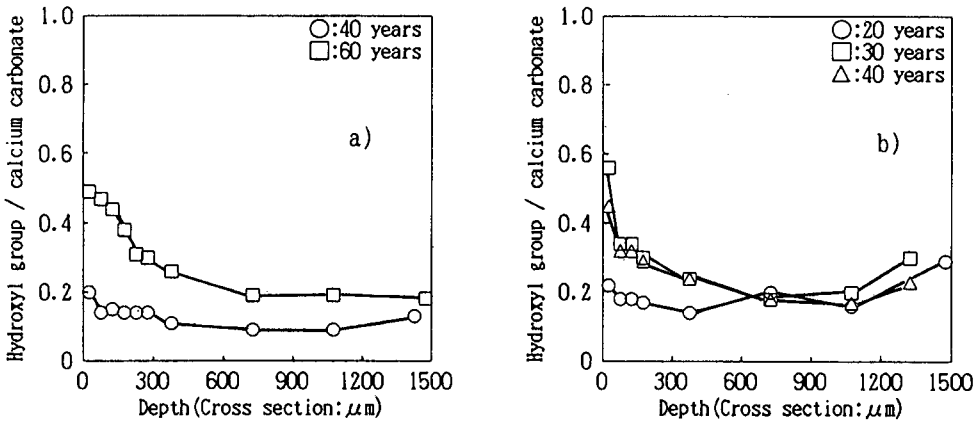

Fig. 6 The ratio of hydroxyl group/calcium carbonate as a function of depth.
a) Radiation aging
b) Combined heat-radiation aging

exposure time of 60 years in the combined heat-radiation aging, it was very difficult to prepare samples due to extraordinary hardening.

From the above results, it is considered that the gel ratio and the plasticizer residual ratio can be utilized as effective parameters to perform degradation diagnosis, because they have shown the remarkable differences depending on the deteriorating conditions and period. At the next step, we will add aging test by heat only. We will then make comparison between material degradations by radiation, heat, and combined heat-radiation aging, so that we can further study the effect of these factors to jacketing materials and establish the effective method for degradation diagnosis.

4. Conclusion

(1) Cross linking reaction becomes larger by combined heat-radiation aging than by radiation aging.
(2) The volume of plasticizer decreases in radiation aging, and much more decrease caused when heat is applied simultaneously.
(3) In the results by thermogravimetric analysis for the samples exposed to the combined heat-radiation aging, the longer the equivalent exposure time is, the smaller the weight loss at temperatures above 350°C.
(4) Property change of calcium carbonate is noted from micro FT-IR analysis, and it is larger at the surface area.
(5) The residual volume of plasticizer and the gel ratio are the two factors in which we noted remarkable differences depending on aging conditions and period. Therefore, there is a possibility to utilize these differences as effective parameters for degradation diagnosis.

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