J Electr Eng Technol.2015; 10(3): 1162-1168
http://dx.doi.org/10.5370/JEET.2015.10.3.1162

ISSN(Print) 1975-0102
ISSN(Online) 2093-7423

Effects of Dried Days on Properties of Seawater and Freshwater Flooded CSPE in NPPs

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Abstract – Accelerated thermal aging of chlorosulfonated polyethylene (CSPE) was performed for 0 days, 80.82 days, and 161.63 days at 100°C, which is equivalent to 0 y, 40 y, and 80 y of aging, respectively, at 50°C. After freshwater flooding, the volume electrical resistivity of CSPE was highest after 180 days of drying, and its insulating property recovered when dried for more than 300 days. The dielectric constant of the CSPE was not measured after seawater flooding. The dielectric constant of the accelerated thermally aged CSPE was higher after freshwater flooding than that before seawater flooding. The bright, open pores of CSPE were converted into dark, closed pores after seawater flooding, and the dark, closed pores of the accelerated thermally aged CSPE samples were partly converted into bright, open pores after freshwater flooding. The apparent density of CSPE increased slightly whereas its elongation at break (EAB) decreased until 80 y of accelerated thermal aging before seawater flooding. The peak binding energies of oxygen in the non-accelerated and accelerated thermally aged CSPE for 40 y and 80 y were shifted by more than 1.0 eV after seawater and freshwater flooding. The CH_2 content in the non-accelerated and accelerated thermally aged CSPE for 40 y and 80 y after seawater flooding for 5 days was lower than that before seawater flooding whereas atoms such as Cl, O, Pb, Al, Si, Sb, and S that are related to conducting ions such as Na^+, Cl^-, Mg^{2+}, SO_4^{2-}, and K^+ were relatively increased.

Keywords: CSPE, Volume electrical resistivity, Dielectric constant, Apparent density, EAB, XPS, XRF

1. Introduction

Countries with advanced atomic energy have been investigating methods for evaluating the aging of cables in nuclear power plants (NPPs) and investing on continued research efforts to explore new approaches [1, 2].

Cables used in NPPs must be designed to last through the plant life owing to the high cost of cable replacement and the complexity of the process. However, cables installed in certain areas such as containment buildings may degrade faster than the normal aging rate, thus affecting cable quality [3, 4].

An optimum degradation evaluation tool that can accurately determine the degree of deterioration of the insulation material or jacket of a cable and recommend an appropriate replacement time has been proposed and improved [5-7]. This method predicts the exact residual life of a cable via suitable condition monitoring.

The jacket of a cable installed in certain areas such as a containment building is exposed to poor surroundings including radioactive rays, steam, temperature, pressure, moisture, and chemical materials and may be submerged [8].

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Received: November 5, 2014; Accepted: January 8, 2015

Chlorosulfonated polyethylene (CSPE) is obtained via simultaneous chlorination and chlorosulfonation of polyethylene. It is a polymer comprising a modified polyethylene backbone with chloro- and sulfonyl chloride side groups. Crosslinking can be achieved by using different curing methods (e.g., sulfur, peroxides, and maleimide) to produce commercial generic Hypalon rubber [4, 9].

Chlorosulfonated polyethylene is an important and widely used rubber and is typically used as a sheathing material for electrical cables employed in nuclear power facilities. It is also used in auto supplies, life-saving equipment, and building materials [10, 11]. In this study, the degree of deterioration of non-accelerated and accelerated thermally aged CSPE samples with number of dried days after seawater and freshwater flooding was determined. The electrical, physical, and chemical properties of non-accelerated and accelerated thermally aged CSPE samples were evaluated through volume electrical resistivity, dielectric constant, apparent density, elongation at break (EAB), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF) analyses.

2. Experimental Procedure

2.1. Sample preparation

A flat-type CSPE of 1-mm thickness (Taihan Electric

Wire Co., Ltd.) was used as standard CSPE. To obtain soaked CSPE, the flat-type CSPE was soaked in seawater for 5 days and then dried for 5 days at room temperature. Further, to obtain cleaned CSPE, the soaked CSPE was cleaned for 5 days with freshwater and dried for 480 days at room temperature. Accelerated thermal aging of a CSPE was performed for 0 days, 80.82 days, and 161.63 days at 100°C, which is equivalent to 0 y, 40 y, and 80 y of aging, respectively, at 50°C, and these samples are referred to as CSPE-0y, CSPE-40y, and CSPE-80y, respectively, henceforth.

2.2. Measurement of volume electrical resistivity

The resistance of a CSPE cable varies with different parameters, such as the shape and size of the insulating material. However, the volume electrical resistivity is not affected by these parameters. The volume electrical resistivity of CSPE is measured using the three-terminal guard-ring electrode (patent number 10-1328994) proposed in [12]. The three-terminal guard-ring electrode is designed as in [13-15] and consists of two parallel-plate electrodes to apply 500 VDC to the CSPE and an additional guard-ring electrode to absorb the leakage current.

2.3. Measurement of dielectric constant

In order to compensate for the dielectric constant of CSPE, the electric capacity of the electrometer was measured as

$$C_E = \frac{C_{ext}(V - V_E)}{V_E}$$

C_{ext}: electric capacity of a known condenser or CSPE [F]
C_E : electric capacity of electrometer [F]
V: applied voltage [V]
V_E: charging voltage of CSPE [V]

As shown in [13-15], if the contactor is switched on, electric voltage is applied to the CSPE. Contrarily, if the contactor is switched off, the charging voltage of CSPE can be measured with the electrometer.

2.4. Physical measurement

Microstructural analysis of CSPE was performed using a field-emission scanning electron microscope (FE-SEM, Hitachi & Horiba/S4800& EDS, Japan). The apparent density of CSPE was measured five times using the Archimedes' method. The EAB of CSPE was measured three times according to the American Society for Testing and Materials (ASTM) standard D412.

2.5. Chemical measurement

Chemical variation in the deteriorated CSPE with respect to the number of drying days was analyzed using a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF, S4 Pioneer, Bruker, Germany) and an X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Scientific, UK).

3. Experimental Results and Discussion

3.1. Volume electrical resistivity

As shown in Fig. 1, the highest volume electrical resistivities of CSPE-0y, CSPE-40y, and CSPE-80y are 7.630×10^{14} Ω·cm, 4.972×10^{14} Ω·cm, and 7.253×10^{14} Ω·cm when dried for 180 days at room temperature. The lowest volume electrical resistivities of the CSPE-0y, CSPE-40y, and CSPE-80y samples are 2.144×10^{13} Ω·cm, 1.570×10^{13} Ω·cm, and 1.924×10^{13} Ω·cm, respectively, when dried for 300 days at room temperature. The volume electrical resistivities of the accelerated thermally aged CSPE samples are lower than those of the non-accelerated thermally aged CSPE samples, thus indicating that the ionic (electron or hole) conduction current increases when the branch chain of the CSPE polymer separates from the main chain of polyethylene owing to the thermal stress of accelerated thermal aging [5]. The insulating property of the CSPE

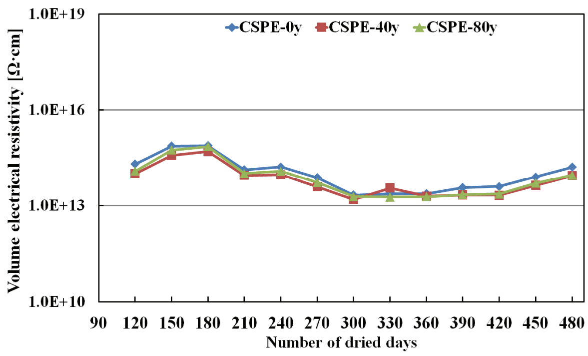

Fig. 1. Variation in volume electrical resistivity of CSPE with number of dried days after seawater and freshwater flooding for 5 days

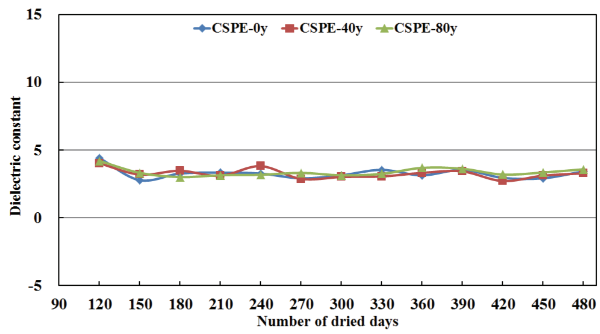

Fig. 2. Variation in dielectric constant of CSPE with number of dried days after seawater and freshwater flooding for 5 days.

soaked in seawater owing to tsunami was recovered between 330 and 480 dried days, and the insulating property of the non-accelerated thermally aged CSPE sample recovered faster than those of the accelerated thermally aged CSPE samples.

3.2. Dielectric constant

As shown in Fig. 2, the permittivities of the CSPE-0y, CSPE-40y, and CSPE-80y samples dried for 120 days at room temperature are 4.422, 4.032, and 4.209, respectively, which are the highest values. The dielectric constant of non-soaked CSPE is 2.856 at room temperature [15]. However, the dielectric constant of the seawater soaked CSPE is not measured. The dielectric constant of CSPE-0y was 4.03 when dried for 1 day, which is higher than that of the non-soaked CSPE sample [13-14]. The ionic polarization of CSPE-0y is caused by Na^{+}, Cl^{-}, Mg^{2+}, SO_4^{2-}, Ca^{2+}, and K^{+} ions because of the salinity of seawater. At room temperature, the dielectric constants of CSPE-0y, CSPE-40y, and CSPE-80y are in the ranges of 4.422–2.786, 4.032-2.722, and 4.209-3.016, respectively. The dielectric constants of CSPE-0y, CSPE-40y, and CSPE-80y decrease slightly as the number of dried days at room temperature, as shown in Fig. 2. Therefore, the number of Na^{+}, Cl^{-}, Mg^{2+}, $SO4^{2-}$, Ca^{2+}, and K^{+} ions in CSPE-0y, CSPE-40y, and CSPE-80y decrease as the number of dried days increase owing to the salinity of the seawater.

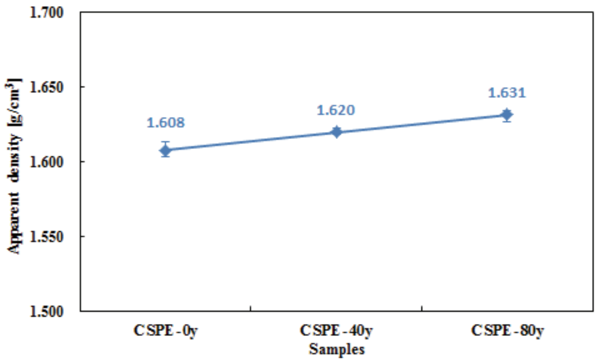

Fig. 3. Variation in apparent density of CSPE with accelerated thermal aging.

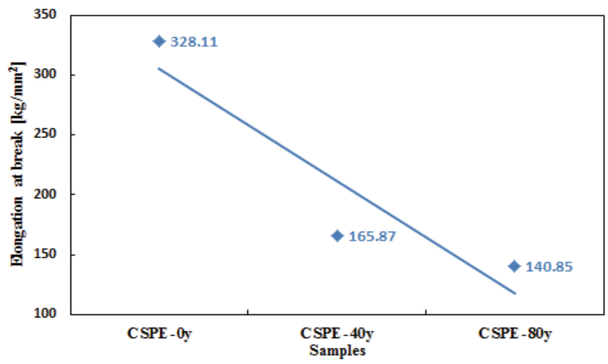

Fig. 4. Variation in EAB of CSPE with accelerated thermal aging.

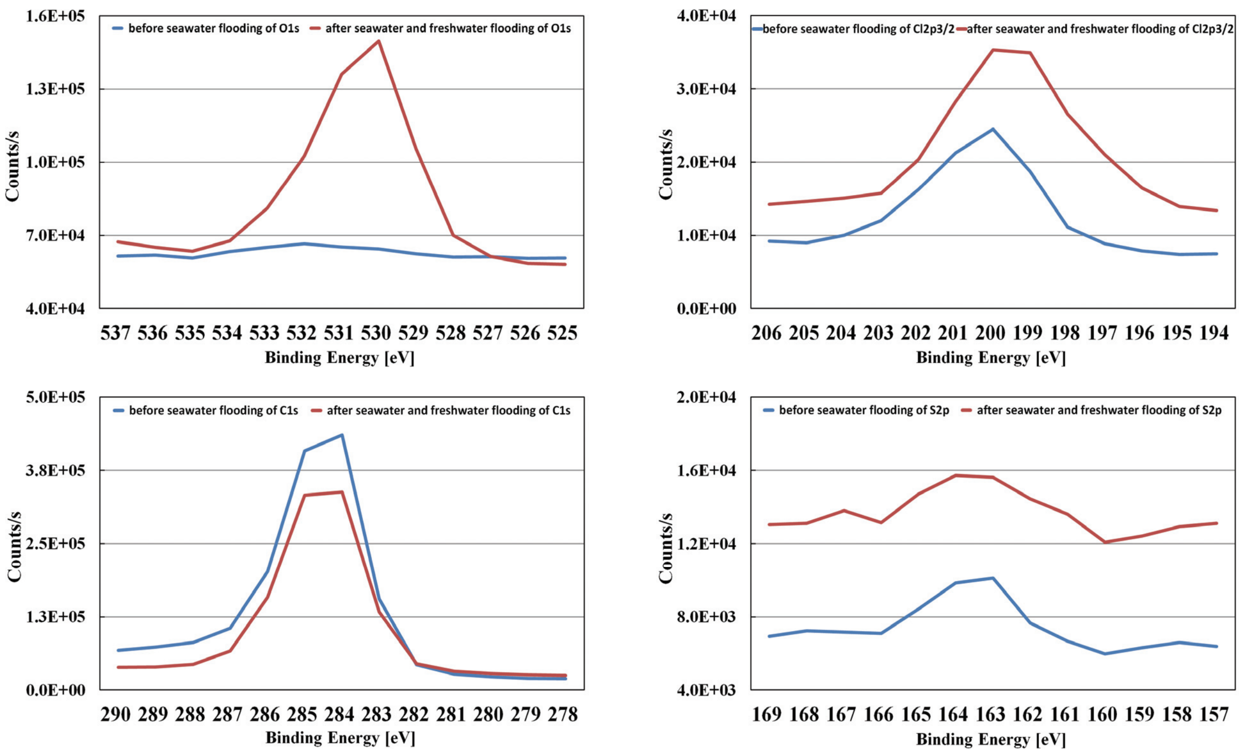

Fig. 5. Binding energy of CSPE-0y

3.3. Physical properties

The bright, open pores of the CSPE-0y sample convert to dark, closed pores after seawater flooding because of salinity, namely, owing to the presence of NaCl, $MgCl_2$, $NaSO_4$, CaCl, and KCl. The dark, closed pores of the soaked CSPE samples partly convert into bright, open pores after freshwater flooding because the salinity of the seawater decreases. As the number of bright, open pores in CSPE increases, the volume electrical resistivity increases, and as the number of dark, closed pores increases, the volume electrical resistivity of CSPE decreases, as was seen in the FE-SEM images [14-15].

Fig. 3 shows the apparent densities of CSPE-0y, CSPE-

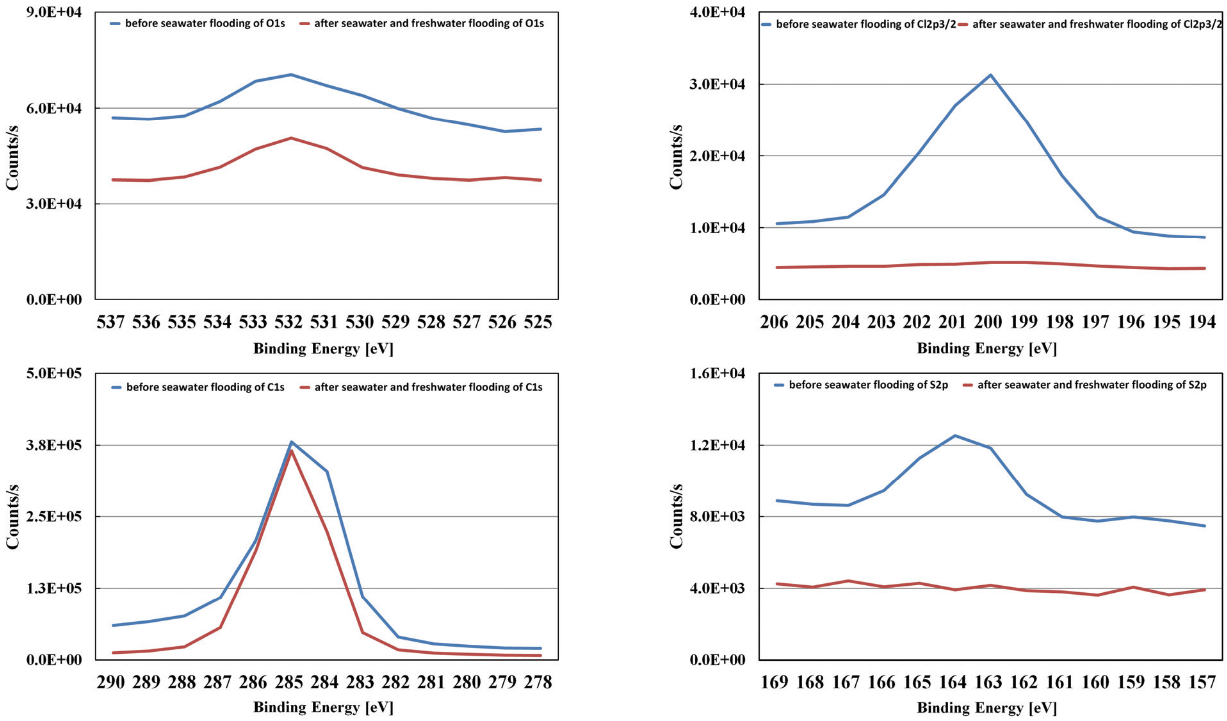

Fig. 6. Binding energy of CSPE-40y.

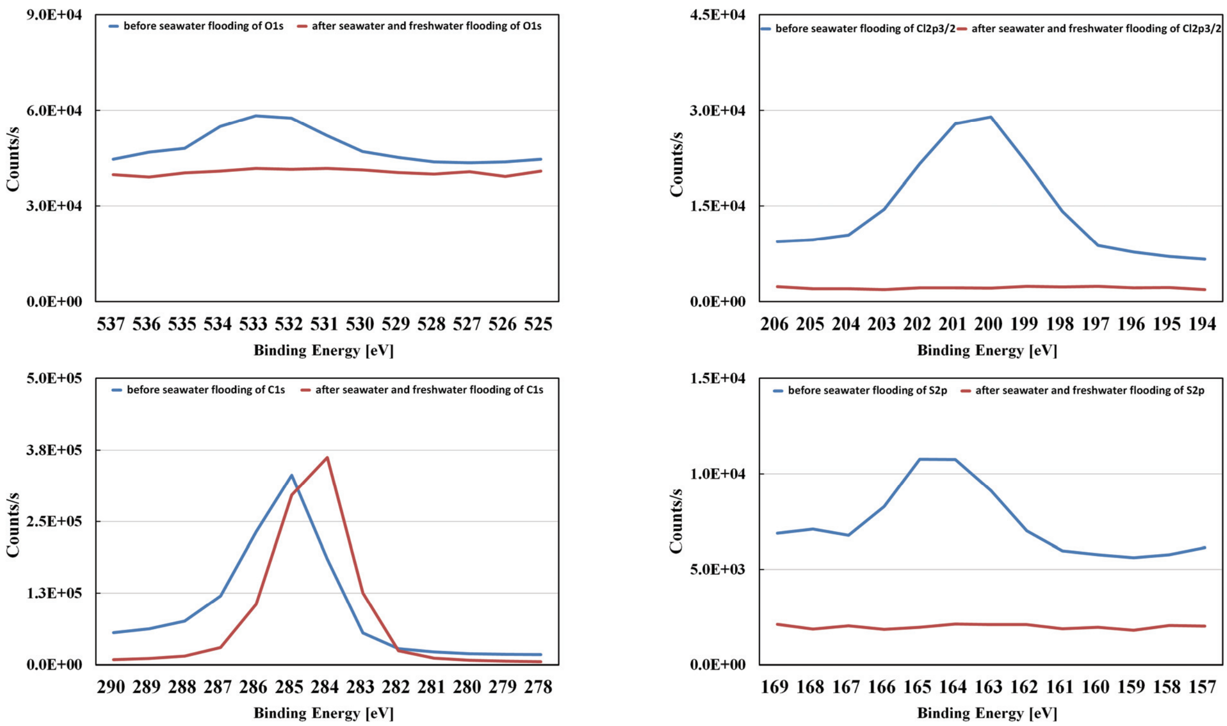

Fig. 7. Binding energy of CSPE-80y.

40y, and CSPE-80y before seawater flooding. As can be seen, the apparent density increases slightly with accelerated thermal aging up to 80 y because of the effect of the degree of thermosetting.

Fig. 4 shows the EAB values of the CSPE-0y, CSPE-40y, and CSPE-80y samples before seawater flooding. We can see that the EAB value decreases until 80 y of accelerated thermal aging because of dependence on the degree of thermosetting. Thermosetting polymers harden permanently when heat is applied to CSPE and do not soften upon subsequent heating.

3.4. Chemical properties

Fig. 5 shows that the peak binding energies of oxygen and sulfur in CSPE-0y shift from 532.08 eV to 530.08 eV and 163.08 eV to 164.08 eV, respectively; therefore, their peak binding energies are shifted by more than 1.0 eV.

As shown in Fig. 6, the peak binding energy of sulfur in CSPE-40y shifts from 164.08 eV to 167.08 eV.

Fig. 7 shows that the peak binding energies of oxygen, carbon, chlorine, and sulfur in CSPE-80y shift from 533.08 eV, 285.08 eV, 200.08 eV, and 165.08 eV to 531.08 eV, 284.08 eV, 199.08 eV, and 164.08 eV, respectively, with a shift of over 1.0 eV.

The binding mechanism of oxygen, carbon, chlorine, and sulfur is altered in the CSPE samples because their reactions are altered owing to salinity.

Figs. 8 and Fig. 9 show XRF analysis data of CSPE-0y, CSPE-40y, and CSPE-80y samples before and after seawater flooding.

As shown in Figs. 8 and Fig. 9, the CH_2 component is reduced in the accelerated thermally aged CSPE samples after seawater flooding for 5 days whereas atoms such as Na, Cl, Mg, O, Pb, Al, Ca, K, Si, Sb, and S, which are related to conducting ions such as Na^+, Cl^+, Mg^{2+}, SO_4^{2+}, Ca^{2+}, and K^+, are relatively increased. The antioxidant additives of CSPE are PbO, Sb_2O_3, $Al(OH)_3$, $Mg(OH)_2$, and $Ca(OH)_2$. Therefore, from XRF analysis, the antioxidant atoms of CSPE are plumbum, antimony, aluminum, and magnesium.

4. Conclusions

The physical, chemical, and electrical properties of accelerated thermally aged CSPE samples were analyzed to determine the degree of deterioration, and the following conclusions can be drawn.

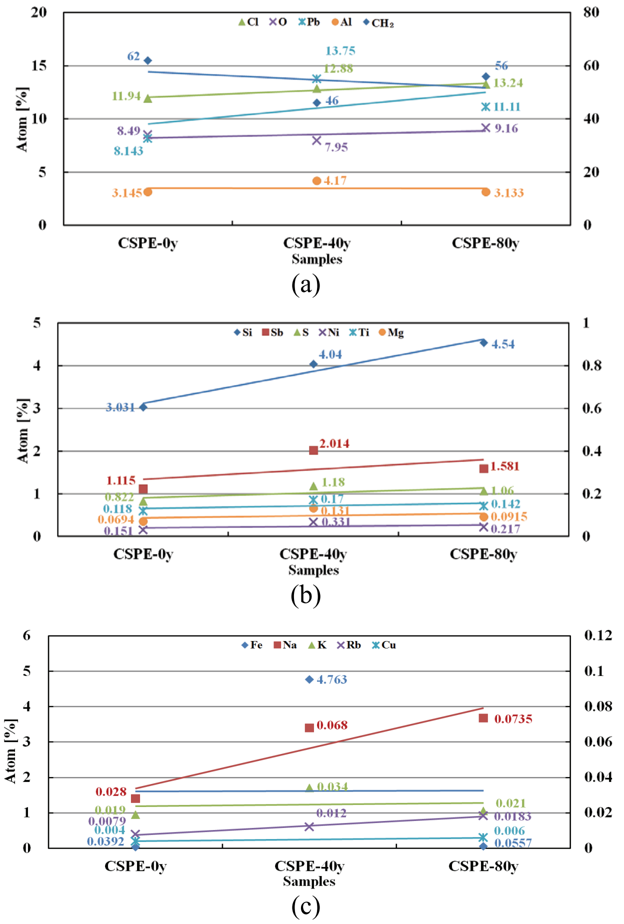

Fig. 8. Percentage of different atoms in CSPE before seawater flooding.

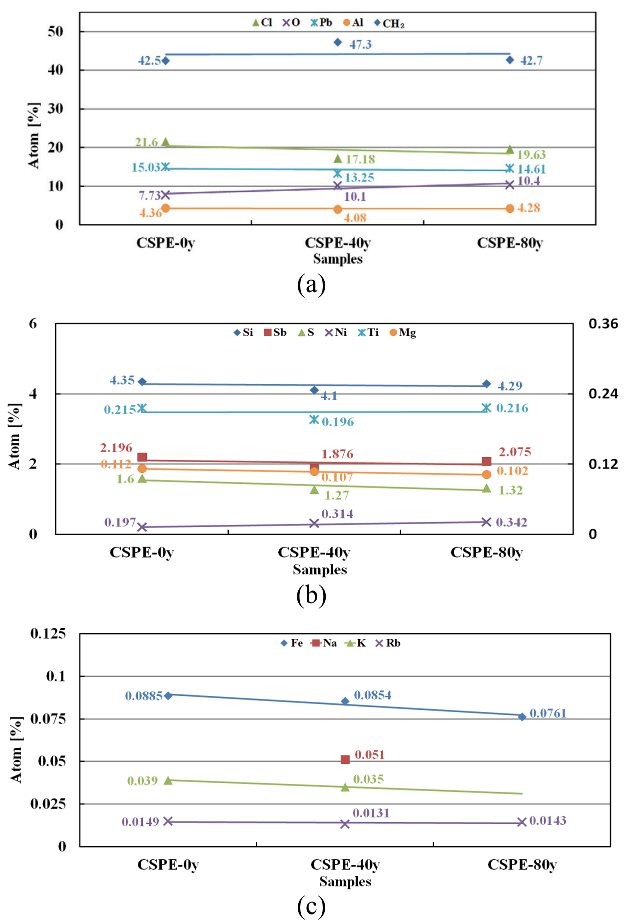

Fig. 9. Percentage of different atoms in CSPE after seawater flooding.

1. The volume electrical resistivity of accelerated thermally aged CSPE is lower than that of non-accelerated thermally aged CSPE, and the insulating property of non-accelerated thermally aged CSPE recovers faster than that of accelerated thermally aged CSPE.
2. The dielectric constant of CSPE decreases slightly as the number of dried days at room temperature increases. Therefore, dielectric constant cannot be used to determine the degree of deterioration of accelerated thermally aged CSPE.
3. The apparent density of CSPE increases whereas the EAB value decreases with increasing number of thermal aging years because of the effect of degree of thermo-setting.
4. The peak binding energies of oxygen, carbon, chlorine, and sulfur in CSPE-80y are shifted by more than 1.0 eV.
5. The XRF analysis shows that the antioxidant atoms of CSPE are plumbum, antimony, aluminum, and magnesium.

The insulation property of cables in NPPs is decreased because of seawater flooding, and the insulation property can be recovered through freshwater flooding. The volume electrical resistivity, peak binding energy, and micro-structural analyses of CSPE suggest evaluating the possibility of the aging state of accelerated thermally aged CSPE based on the EAB and apparent density. Volume electrical resistivity, peak binding energy, atom analysis, EAB, and apparent density can be used as evaluation tools to determine the degree of deterioration of insulation material or jacket of a cable and find the appropriate replacement time.

Acknowledgements

This paper was supported by Wonkwang University in 2015.

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