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Effect of Gamma Radiation on Degradation Behavior of Polymeric Materials

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1. Introduction

After severe accidents (SA) in Three Miles Island and Fukushima Daiichi nuclear power plant (NPP), functionality of safety-related equipment to mitigate of accident effects has become more important in SA environment. In SA, high temperature and high dose radiation environments were generated. Therefore, according to 10CFR50.34, SECY-90-016 and -93-087, safety-related equipment to prevent or mitigate the accident effects are must perform their functions in required periods in SA environments (temperature, radiation, and pressure, etc.). [1].

Polymeric materials in NPP are used as cable, seal, and switches. Polymeric materials have been reported to be relatively vulnerable to radiation environment compared to metallic materials. The polymeric materials are widely used in industrial fields in high temperature environment, it has been studied in nuclear power generation as well as in other industrial fields. However, more studies are required gamma-irradiation effect on degradation. High dose gamma radiation is generated in the normal operation and accident environment of NPP. Gamma radiation induced degradation mechanisms based technical methods and test procedure of quantitative assessment of degradation level of polymeric materials exposed to the radiation are not well established. Therefore, it is important to evaluate the degradation behavior of polymeric materials in radiation environment to evaluate the equipment survivability of safety related equipment. [2-3]

In this study, gamma radiation induced degradation behavior was investigated by gamma irradiation test and materials properties analysis with four polymeric materials, fluoroelastomer (FKM) green and black grade, ethylene propylene diene monomer (EPDM), and nitrile butadiene rubber (NBR). Mechanical (Shore A hardness) and thermal properties (5% weight loss temperature) were measured by hardness measurement device (shore A hardness) and thermogravimetric analyzer (TGA) to evaluate the degradation behavior in various irradiation dose. And the Fourier transformed infrared (FT-IR) spectroscopy analysis was conducted to investigate the change of molecular structure and chemical bonds of polymeric materials.

2. Experiment

2.1 Gamma-irradiation test

Gamma-irradiation tests were conducted with Co^{60} and dose rate of 9 kGy/hr at the room temperature in the air. According to IEEE-323, the tests were performed at doses from 0 kGy to 2000 kGy, which can occur during normal operation conditions and accident environment of NPP. And mechanical and thermal properties of polymeric materials were measured at 400 kGy. In addition, the tests were conducted by a total integrated dose (TID) of 200 kGy to simulate the normal operating condition.

2.2 Mechanical and thermal properties measurement

The mechanical properties of durometer shore A hardness was measured with Techlock GS-719N according to ASTM D2240.

Between 5 and 20 mg of sample in using ceramic crucible were analyzed through thermogravimetric analyzer using a TA Q500. The analysis was conducted using temperature range of 298 to 900 K with a ramp rate of 10 K/min in N_2. 5% weight loss temperature of fluoroelastomer were obtained to evaluate the change of thermal stability due to gamma radiation.

2.3 Molecular structure analysis

FT-IR spectra were collected using a Nicolet iS50 FT-IR spectrometer with a germanium attenuated total reflectance (ATR) attachment. The spectroscopic analysis was performed with wavelength from 650 to 4000 cm^{-1}, at a resolution of 4 cm^{-1} and with an accumulation of four scans.

3. Results and discussion

3.1 Mechanical and thermal properties

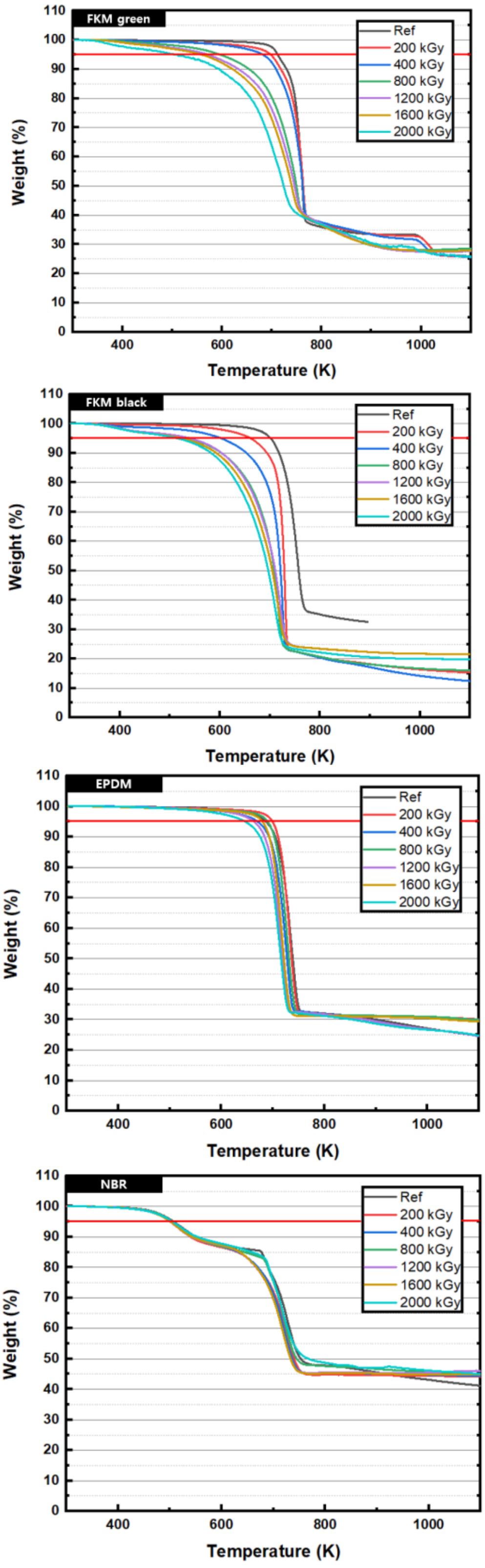

Fig 1. Results of thermogravimetric analysis of irradiated polymeric materials

Hardness measurement and thermogravimetric analysis were performed to investigate degradation of mechanical, thermal properties in various radiation dose condition. As shown in Fig. 1, although there was difference in each polymeric material, faster pyrolysis behavior was observed at higher radiation dose. 5% weight loss temperature of polymeric materials with dose variation in Fig. 2. The 5% weight loss temperature of FKM green and black of fluoroelastomer series decreased as the dose increased. However, the change in EPDM and NBR was relative not significant.

The thermal stability decreased because free radicals generated from radiation induced scission of chemical bonds and unstable structure. The free radical reacted with other radical or scissioned molecules to form unstable crystal and decrease crystallinity of polymeric materials. The unstable structures generated by these mechanisms are relatively vulnerable to heat. Because of dehydrofluorination reaction in irradiated FKM green and FKM black, the thermal stability decreased significantly. Free radicals form carbonyl group by auto-oxidation reaction with oxygen, which affects the increases of hardness of polymeric materials.

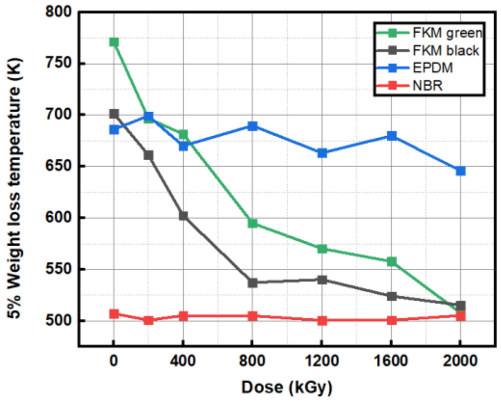

Fig 2. 5% weight loss temperature of irradiated polymeric materials

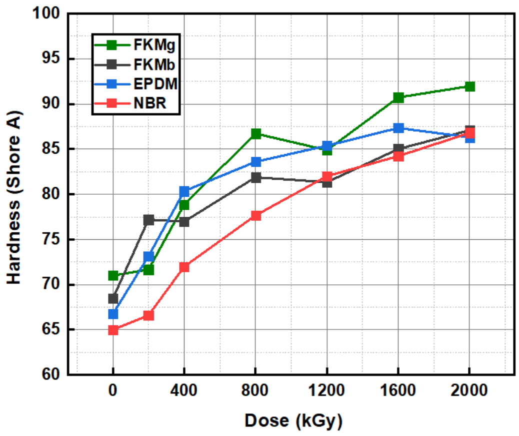

Fig 3. Hardness of irradiated polymeric materials

3.2 Molecular structure analysis

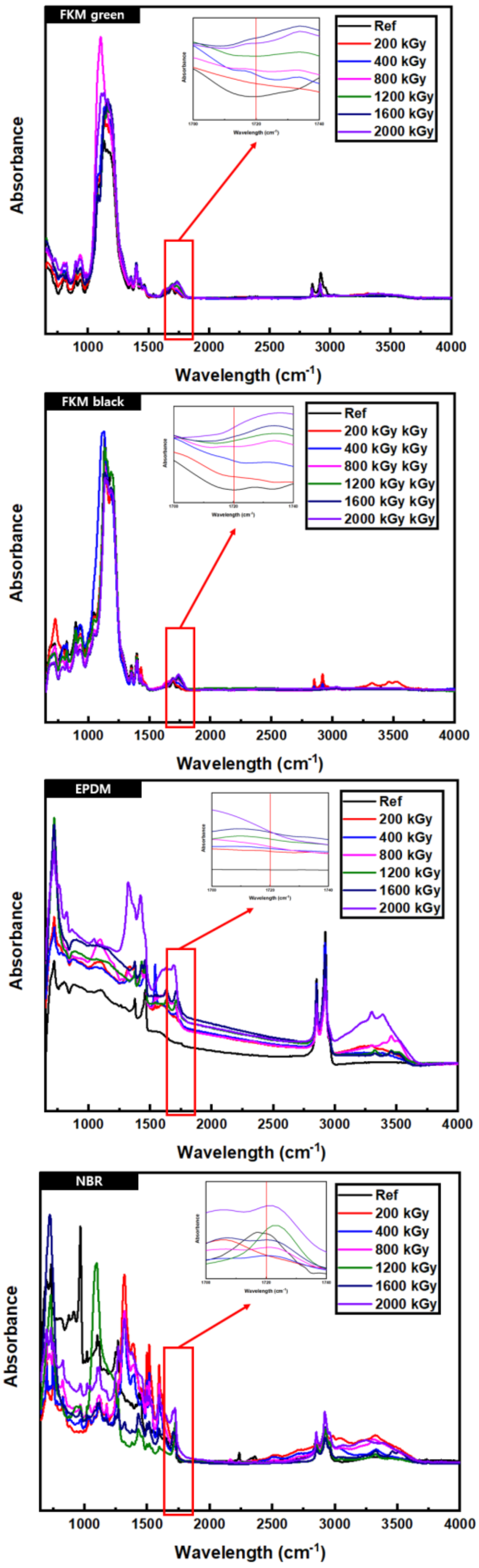

Fig 4. FT-IR spectrum of irradiated polymeric materials

The FT-IR spectra of polymeric materials after irradiation can be seen in Fig 4. The peak of wide and strong intensity at 1100-1300 cm^{-1} in FKM green and FKM black indicate that the C-F bond and C-H bonds (750 and 820 cm^{-1}) appeared. In EPDM case, the C-H peak appears strongly in the 2800-3000 cm^{-1} range, and the peak of S=O increases in the 1300-1400 cm^{-1} range as the dose increases.

The carbonyl groups (C=O) were generated at 1720 cm^{-1} after irradiation, which caused mechanical hardening. As shown in Fig 4 and 5, C=O bonds increased with dose increasing. This is because free radicals generated by the break of the C-H bond react with oxygen in the atmosphere to form C-O and C=O. [4]. The mechanical properties analysis showed that the phenomenon significantly increased hardness of the polymeric materials. Therefore, increasing of C=O bonds by radiation affects the degradation of polymeric materials. [5].

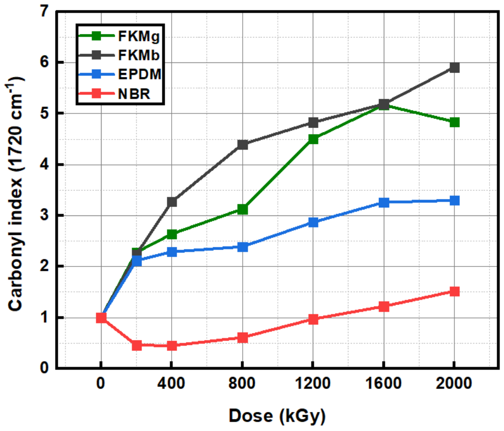

Fig 5. Carbonyl index (1720 cm^{-1}) of irradiated polymeric materials

3. Conclusion

In this study, various gamma-irradiation condition includes the normal operating condition and accident environment were simulated to investigate the effects of radiation on the degradation of polymeric materials. To investigate the degradation behavior of mechanical and thermal properties were measured, and FT-IR analysis was conducted to obtain the spectrum which indicates the change of chemical bonds.

After the irradiation, polymeric materials were hardened significantly. And thermal stability also degraded. This degradation phenomenon occurs because free radicals generated by radiation react with oxygen in the air to form C-O and C=O. The C=O increased from C-O bonds generated in the irradiation under normal operating conditions and the free radicals generated from the scissioned bonds of C-H after irradiation under severe accident environment, which causes hardening of the polymeric materials

In conclusion, the radiation induced degradation under normal operating conditions and accident radiation environment cause the hardening of the polymeric materials in NPP. Therefore, to ensure equipment survivability of safety-related equipment, including polymeric seal or cable insulation, should be designed based on understanding and experimental results of degradation behavior of polymeric materials.

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