Study of Gamma Irradiation Effect on Mechanical properties and structure of Nitrile Butadiene Rubber and Ethylene Propylene Diene Rubber

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1. Introduction

After severe accidents in Three Miles Island and Fukushima Daiichi, functionality of safety-related equipment to mitigate of accident effects has become more important in SA (severe accident) environment. In SA, high temperature and high dose radiation were generated. The hydrogen was generated form damaged fuel cladding and coolant water. And the hydrogen burned to create high temperature environment. 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 period in SA environment (temperature, radiation, and pressure, etc.). [1]. Polymeric materials in safety-related equipment such as cable and valve are more vulnerable compare to metallic components in accident environment. Therefore, to ensure the survivability and functionality of safety-related equipment, the assessment of polymeric materials must be performed. Therefore, to investigation of degradation of polymeric materials is very important to ensure the safety of NPP. [2].

In this study, behavior of mechanical properties and structure analysis of gamma irradiated nitrile butadiene rubber (NBR) and ethylene propylene diene rubber (EPDM) were investigated. Polymer samples specimens are exposed to various gamma irradiation of 200, 400, 800, 1200, 1600, 2000 kGy. To investigate the degradation behavior in molecular structure, Fourier transformed infrared (FT-IR) spectroscopy was performed.

2. Experimental

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 properties measurement

The mechanical properties were measured using tensile test and hardness measurement. The elongation at break (EAB) and tensile strength (UTS) were measured. According to ASTM D412, the specimens were prepared type C, crosshead speed of 50 mm/min using a self-tightening grip and Instron 8801. And durometer shore A hardness were measured according to ASTM D2240

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 Properties

In the case of NBR, EAB decreased as the gamma radiation dose increased. However, the UTS hardly changed despite increasing the dose. EPDM showed a tendency to decrease with increasing gamma radiation dose in both UTS and EAB. Hardness increased with increasing gamma radiation dose for both NBR and EPDM. Based on these results, gamma radiation causes hardening of NBR and EPDM. This phenomenon is because when gamma radiation is irradiated with molecules, the bonding of the function groups bonded to the branch is weakened or broken. Free radicals are generated from scissioned function groups, and this trend is accelerated from unstable structures that abstract hydrogen. As a result, the unstable molecules combine with other molecules and crosslinking to form a three-dimensional network occurs. Because of difference of the thermodynamic compatibility, weak links were formed at the interface between stable structure and irradiated molecular, which reduced the mechanical properties. EPDM has many branches that are bonded to the main chain, there are relatively more sites affected by irradiation than NBR. Therefore, the mechanical properties of EPDM decreased due to the thermodynamics compatibility of the phase than the hardening effect due to the increase in molecular weight and crystalline phase due to crosslinking. In case of NBR, the tensile strength was almost unchanged as the two effects were canceled, but the interface area that hindered stretching increased, so the elongation decreased as the dose increased. [3].

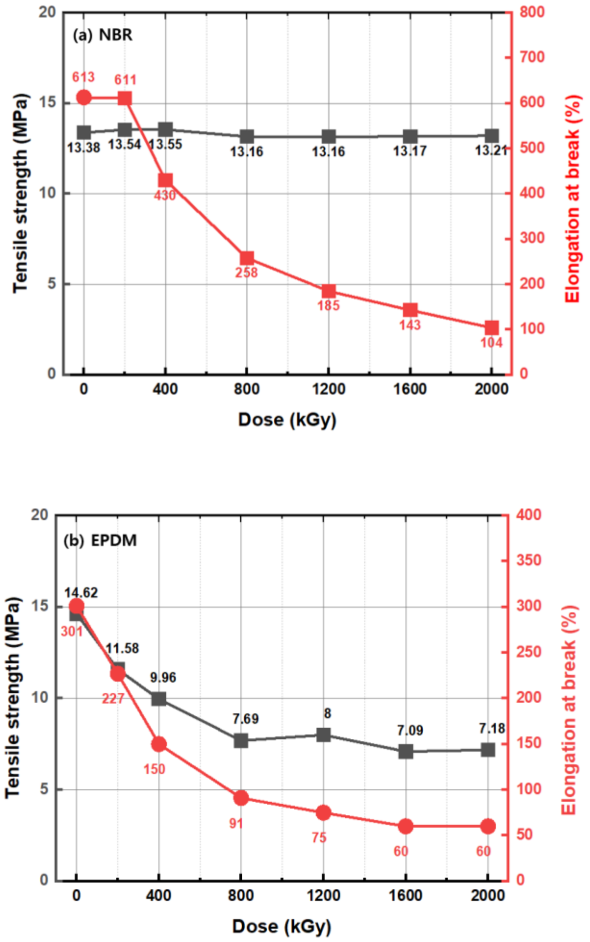


Fig 1. Tensile properties of gamma irradiated polymer (a) NBR and (b) EPDM

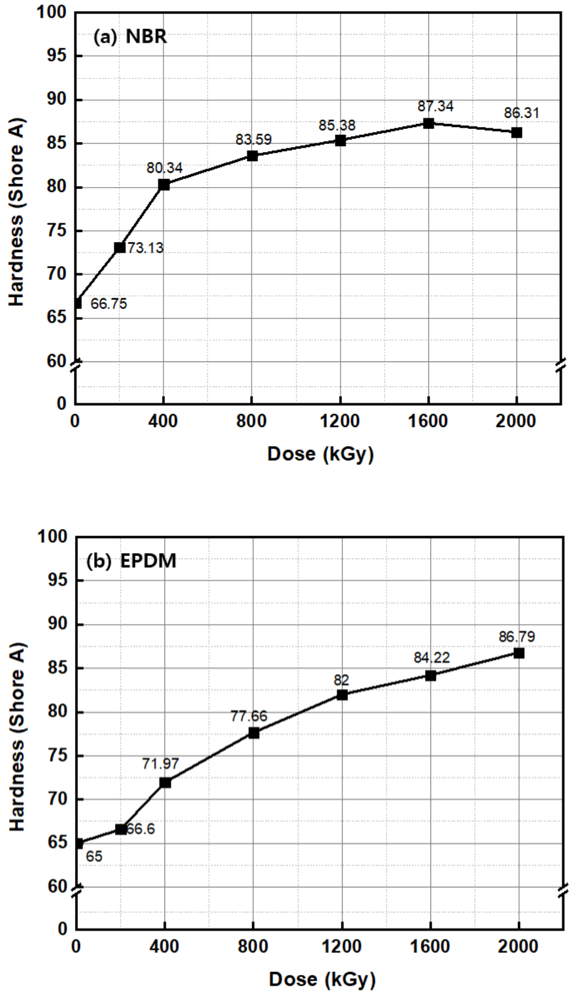


Fig 2. Shore A hardness of gamma irradiated polymer (a) NBR and (b) EPDM

3.2 Fourier Transformed Infrared Spectra

The infrared absorption spectra for the polymer samples are shown in Fig. 3. The absorbance peaks of 965 and 2233 cm-1 indicate the function group of the carbon-carbon double bonds (1, 4 trans bonding) and the nitrile group, respectively. And because of irradiation and thermal degradation, hydroxyl group (3350 and 1440 cm^{-1}) and carbonyl group (1720 cm^{-1}). C=O bond were formed by reacting with oxygen in atmosphere at this site. And scission of functional group generated free radicals. Crosslink increased due to formation of link between molecular structure by free radicals. The double bonds and crosslink density, such as C=O are known to affect the mechanical properties of polymeric materials. As shown in Fig 4, carbonyl index using normalized C=O peak intensity (1720 cm^{-1}) increased with gamma radiation dose increasing. [4-5].

As a result of correlation analysis, this tendency of CI increasing affects the mechanical properties. In the case of EPDM, the carbonyl index was analyzed to be closely related to the mechanical properties, and in the case of NBR, the correlation factor was greater than 0.9 at points excluding 0 and 200 kGy. Based on these analysis results, it is possible to predict the tendency of mechanical properties of gamma irradiated NBR and EPDM through the carbonyl index.

$$Correl(X,Y) = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{\sum(x-\bar{x})^2\sum(y-\bar{y})^2}}$$

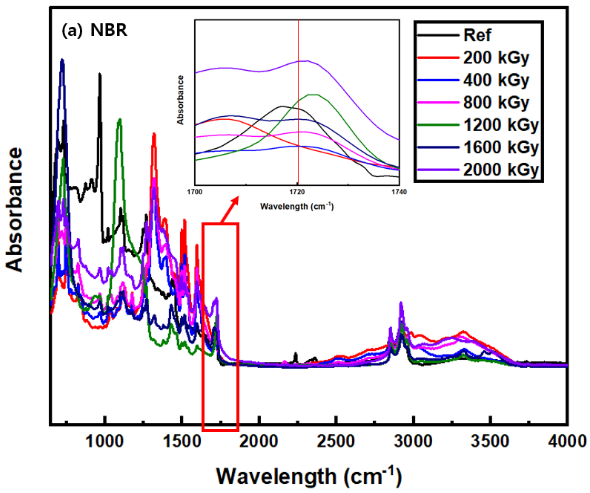
Table 1 : Correlation analysis result between carbonyl index and mechanical properties of NBR and EPDM

Carbonyl index		
Dose (kGy)	EPDM	NBR
0	1.00	1.00
200	2.12	0.46
400	2.29	0.45
800	2.39	0.61
1200	2.87	0.97
1600	3.26	1.22
2000	3.30	1.52

hardness		
Dose (kGy)	EPDM	NBR
0.00	65.00	66.75
200.00	66.60	73.13
400.00	71.97	80.34
800.00	77.66	83.59
1200.00	82.00	85.38
1600.00	84.22	87.34
2000.00	86.79	86.31
Correlation	0.9201	0.38388

EAB		
Dose (kGy)	EPDM	NBR
0.00	301.00	613.00
200.00	227.00	611.00
400.00	150.00	430.00
800.00	91.00	258.00
1200.00	75.00	185.00
1600.00	60.00	143.00
2000.00	60.00	104.00
Correlation	-0.9384	-0.6278

UTS		
Dose (kGy)	EPDM	NBR
0.00	14.20	13.38
200.00	11.58	13.54
400.00	9.96	13.55
800.00	7.69	13.16
1200.00	8.00	13.16
1600.00	7.09	13.17
2000.00	7.18	13.21
Correlation	-0.9376	-0.6404



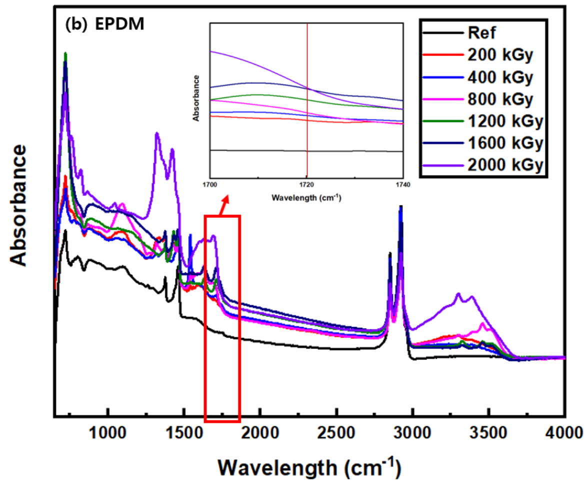


Fig 3. FT-IR spectrum of gamma irradiated polymer (a) NBR and (b) EPDM

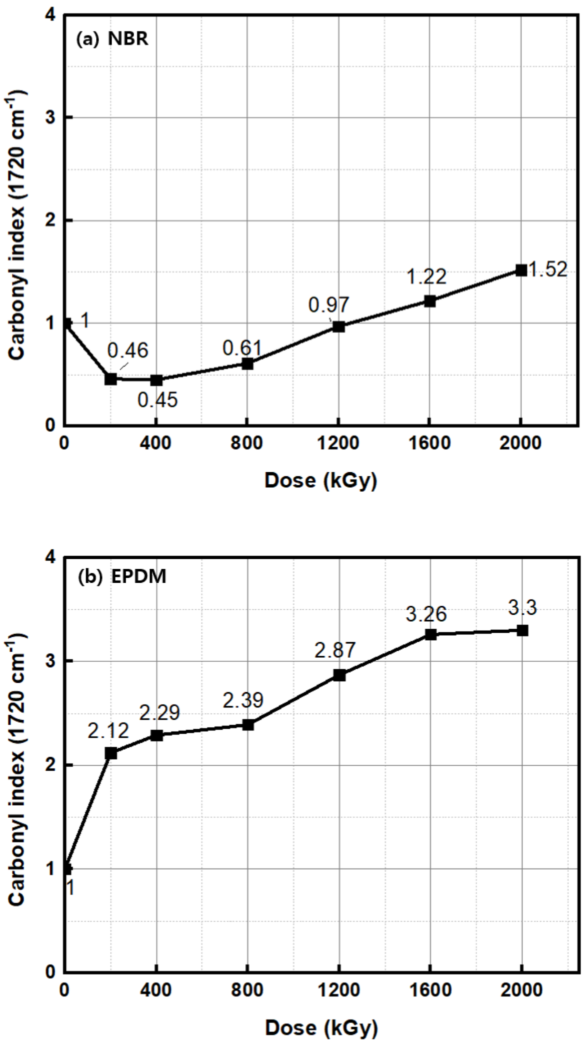


Fig 4. Carbonyl index (1720cm^{-1}) of gamma irradiated polymer: (a) NBR and (b) EPDM

Conclusion

The degradation behavior of NBR and EPDM were investigated using carbonyl index and mechanical properties under gamma radiation with various dose. As the gamma radiation dose increased, hardening occurred, and this phenomenon is because gamma radiation acted as an initiator to scission bonding of function groups inside the molecular. The unstable molecular scissioned function group combines with oxygen in the atmosphere and C=O is generated. As a result of correlation analysis, it is thought that the carbonyl index has a certain relationship with the mechanical properties of NBR and EPDM.

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