

Thermal Stability of Nitrile Butadiene Rubber in Simulated Severe Accident Environments

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1. Introduction

During severe accident (SA) in nuclear power plant, hydrogen was generated by reaction between high temperature corrosion of damaged fuel and coolant water. The hydrogen accumulates inside the containment building and burn when the explosive limit is exceeded. In this situation, high temperature and pressure, high dose radiation environment is generated. This environment can affect the performance of safety-related equipment to prevent or to mitigate the impact of accidents. Polymeric components, such as cables and seals, are used in the safety-related equipment, and are more vulnerable to high temperature and radiation compared to metallic components. Therefore, to ensure the survivability and functionality of safety-related equipment, the degradation assessment of polymeric materials is very important. [1].

In this study, degradation behavior of thermal stability of nitrile butadiene rubber (NBR) in normal operation condition and SA environment was investigated. To simulate the degradation effect, irradiation tests, accelerated thermal aging and thermal degradation tests in SA environment were performed sequentially. Degraded NBR samples were analyzed by thermogravimetric analysis (TGA) to investigate the thermal stability behavior. And change of molecular structure were investigated by Fourier transformed infrared (FT-IR) spectroscopy.

2. Experiment

2.1 Degradation test

NBR sample were irradiated gamma radiation using Co^{60} and dose rate of 9 kGy/hr at the room temperature in the air. Irradiation tests were conducted using radiation dose with 200 and 2000 kGy to simulate total integrated dose (TID) of normal operation condition and severe accident environment, respectively, according to IEEE-323. [2]. Accelerated thermal aging and thermal degradation test to simulate the severe accident temperature profile were performed. The accelerated thermal aging condition was determined by Arrhenius equation, maximum operating temperature, and

operating period. The aging was conducted at 48.9 °C for 804.08 hours to simulate the operating condition of 127.1 °C for 60 years using activation energy of 0.84 eV. To simulate the SA environment, a stored histogram was used to expose the NBR sample to the temperature profile suggested in the previous study. To investigate the environmental factor in normal and severe accident condition, the sequential test matrix was derived as shown in Fig 1. [3].

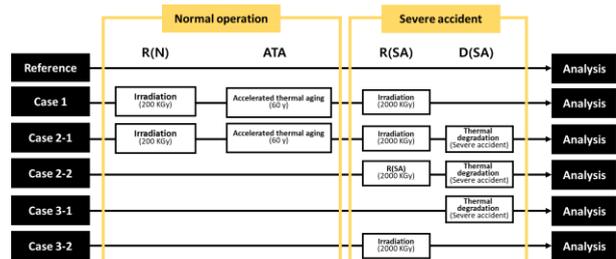


Fig 1. Test matrix for degradation tests in normal operation and severe accident environment.

2.2 Characterization

Thermograms were obtained by thermogravimetric analyzer (TGA TA Q500). The measurement was performed under heating rate of 10 °C/min at a temperature range 25 to 900 °C in nitrogen. About 5-10 mg of samples was used for the TGA. Thermal decomposition activation energy was measured by thermogravimetric analysis according to ASTM E1641 using Flynn-Wall methods as shown in Fig 2. The Flynn-Wall method is simple methods for determining activation energy from weight loss vs temperature data obtained in various heating rates. Flynn-Wall methods using a point of equivalent weight loss, a plot of $\ln \beta$ vs $1/T$ is constructed. The slope of this line plot is used to calculate activation energy (E_a). [4].

$$\ln \beta = \ln \left(\frac{Z E_a}{R} \right) - \ln F(\alpha) - \frac{E_a}{RT}$$

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.

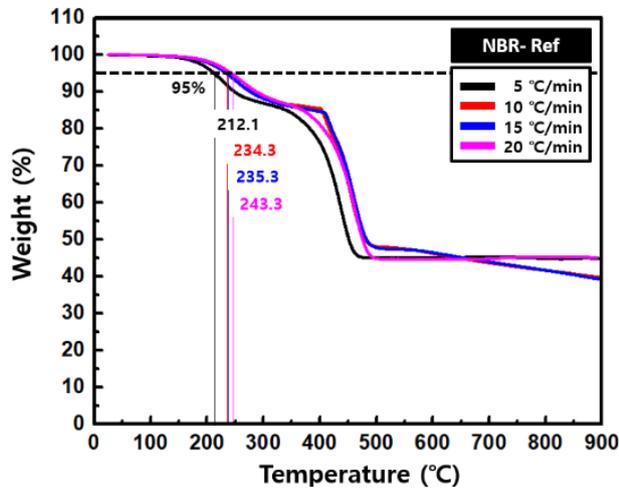


Fig 2. Thermograms in various heating rate (5, 10, 15 and 20 $^{\circ}\text{C}/\text{min}$) to measurement thermal decomposition activation energy of NBR.

3. Results and discussion

3.1 Thermogravimetric analysis

In general, the TGA curve of NBR, first step thermal degradation occurs about 180 $^{\circ}\text{C}$ accompanied by volatilization and weight loss. In first step thermal degradation, water is generated from hydrogen and oxygen in the NBR polymer group and evaporates, resulting in weight loss. Second step thermal degradation occurs at about 300 $^{\circ}\text{C}$, which causes the function group inside the NBR polymer to scission, and after about 470 $^{\circ}\text{C}$, the third step thermal degradation occurs that breaking the main polymer chain. [5].

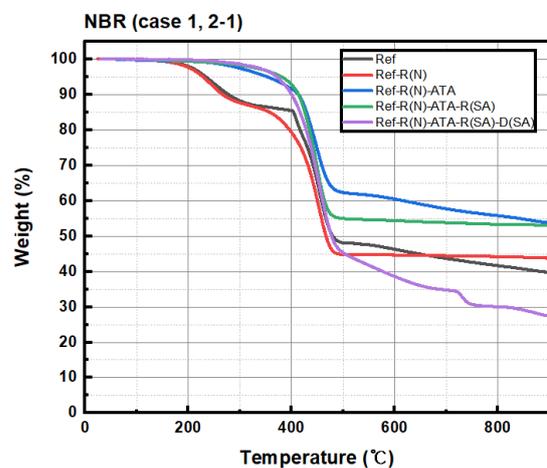
The TGA curves for cases 1 and 2-1 including degradation under normal operating conditions and cases 2-2 to 3-2 that degradation only under SA environment are shown in fig. 3. In the TGA analysis results of NBR, the first step thermal degradation did not occur in accelerated thermal aging (ATA) under normal operation conditions and degradation tests in SA temperature profiles, D(SA). This is because dehydration reaction has already occurred in ATA and D(SA), therefore weight loss due to water evaporation has not occurred.

In the TGA curve in case 2-1, the weight loss due to second thermal degradation was different depending on the test conditions. NBR sample in R(N), irradiation with a dose of 200 kGy, more weight loss occurred due to the second thermal degradation. Free radicals are formed by scission of chemical bonds in function groups due to radiation. These radicals combine with oxygen in

molecular structure, the atmosphere and other radicals to form unstable molecules and abstract hydrogen from other polymers. Therefore, unstable structure is vulnerable by heat, and weight loss was occurred by volatilization. However, weight loss effect by second thermal degradation decreased after ATA. This is because unstable function group and radicals decreased due to annealing in post-irradiation effect in below the first thermal degradation temperature. After D(SA), thermal energy is transferred in molecule to cause scission chemical bonds in the function group. Therefore, unstable function group and radicals are formed and volatilize in the second thermal degradation, resulting in weight loss occurred. Weight loss behaviors due to first and second step thermal degradation in case 2-1, 3-1 and 3-2 showed a large difference according to test conditions. After R(SA), second step thermal degradation behavior in TGA curve almost similar to the reference case. However, the second step thermal degradation temperature of case 2-1 was higher than that of reference and R(SA) samples, and the weight loss effects were higher than in case 3-2. In case 3-2, the starting temperature of thermal degradation in the TGA curve is higher due to crosslinking by radical formation in R(SA) and volatilization in D(SA), but due to the unstable structure more weight loss occurred.

In the samples after R(N) and R(SA), after about 470 $^{\circ}\text{C}$, third step thermal degradation occurred relatively little because volatile elements inside the structure are almost evaporated due to radicals generated by irradiation. After the ATA and D(SA) tests, the final weight loss was almost same, but the weight loss was occurred. Oxygen and hydrogen in atmosphere diffused in the molecular structure during the thermal aging tests, and evaporated, resulting in total weight decreased.

Fig. 4. shows the 5% weight loss temperature that evaluates the bulk thermal stability of the materials. Because of evaporation of volatilization during ATA, 5% weight loss temperature increased after ATA. Therefore, the weight loss due to evaporation did not occur in the TGA curve, and the first step thermal degradation temperature increased by crosslinking. [6].



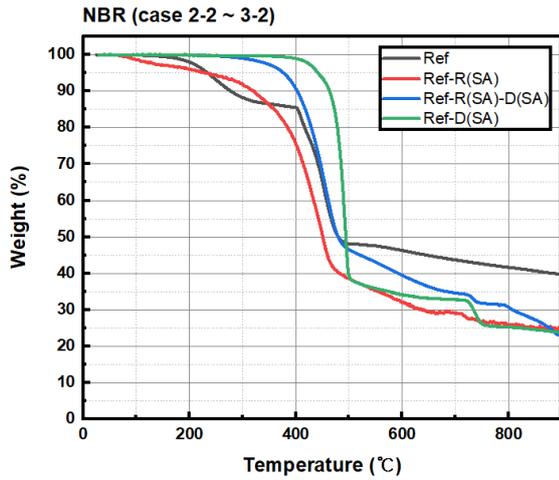


Fig 3. Thermogravimetric curve of NBR after various degradation cases

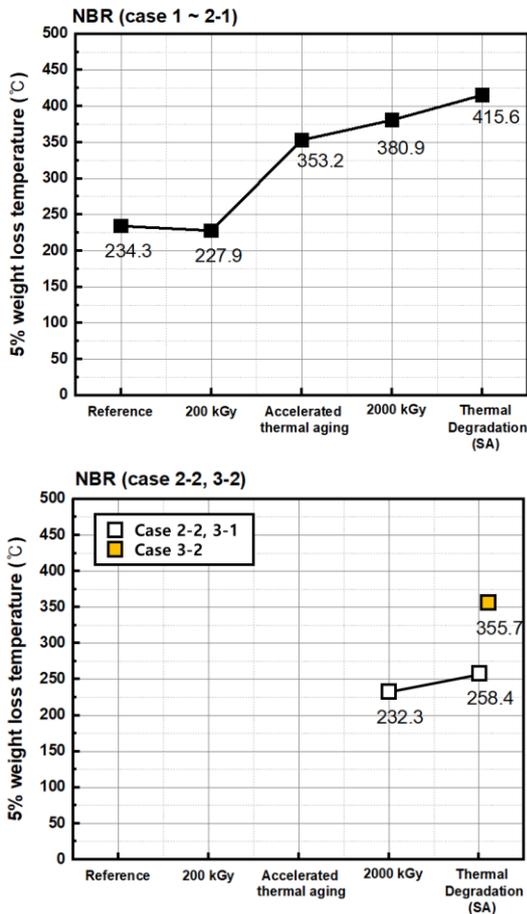


Fig 4. 5% weight loss temperature of NBR after various degradation cases.

3.2 Fourier Transformed Infrared Spectra

The infrared absorption spectra for the NBR samples are shown in Fig. 5. 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 (1719 cm^{-1})

After irradiation, R(N) and R(SA), the molecular weight decreased due to volatilization and chemical bonds was scissioned. Therefore, C-H group decreased by scission and carbonyl and hydroxyl groups increased due to the reaction between radicals generated by irradiation and oxygen in the molecular structure and atmosphere, auto-oxidation reaction. The hydroxyl groups generated by irradiation, combined other hydrogen other molecular and dehydration occurred. hydrogen abstracted structure can be easily crosslinked other molecules. After thermal degradation, ATA and D(SA), peak intensity was hardly observed. This phenomenon can be occurred due to almost the intermolecular bonds was scissioned and decomposed from radiation peak. [7].

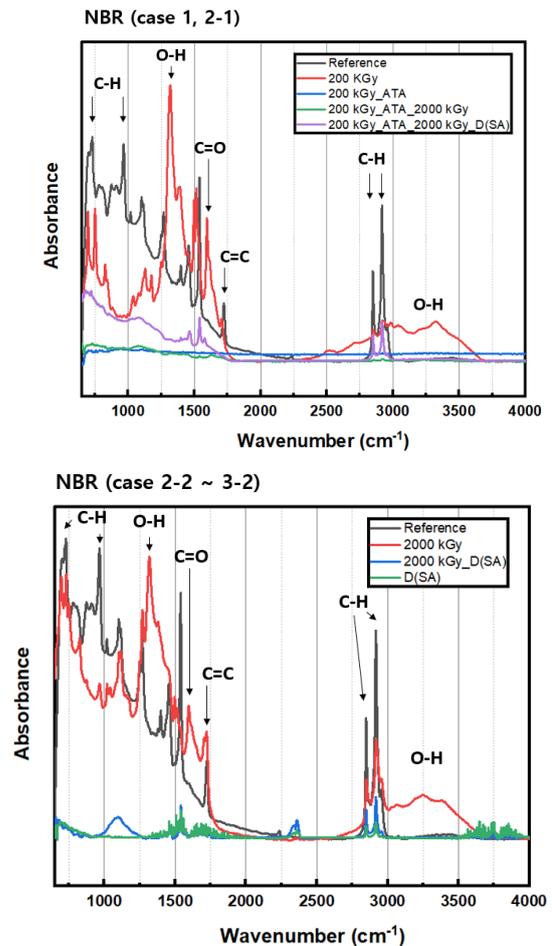


Fig 5. Fourier transformed infrared spectra of NBR

4. Conclusion

In this study, the thermal stability of NBR in normal operation condition and SA environment was investigated by degradation tests and measurement of thermogravimetric curve and molecular analysis using FT-IR spectroscopy.

Irradiation with 200 kGy has little effect on the thermal stability of the NBR. However, it forms hydroxyl groups. These hydroxyl groups act as hydration sites. Hydrogen abstraction due to hydration causes crosslinking in the thermal degradation step, affecting thermal stability. A similar trend was observed in the irradiation with 2000 kGy, and in thermal aging under normal operation and severe accident environment, thermal stability increased by crosslinking.

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