

## Study on Degradation of NBR under Simulated Post-Accident Environment of Severe Accident

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### 1. Introduction

Severe accident (SA) including damage to the reactor core were not considered significantly in terms of safety due to extremely low probability of occurrence. After accidents in Three Mile Island and Fukushima Daiichi, the international electrotechnical commission (IEC) and institute of electrical and electronics engineers (IEEE) recognized the need for qualification of equipment survivability in a SA environment and suggested that regulation is required (IEC/IEEE 60780-323). In the US, regulation such as 10CFR50.34(f), SECY-90-016, and SECY 93-087 require equipment survivability assessment. For equipment survivability, there are methods that 1) compare with equipment qualification data of vendors or suppliers, 2) analysis-based verification using thermal lag analysis, or qualified life analysis and 3) alternative methods such as relocation and installation of fire protection wrap. However, to ensure the functionality of safety-related equipment and component for safety shutdown and mitigation of accident effects, evaluation through type testing under SA environment. [1, 2]

Currently, the assessment of equipment survivability under SA environment has been performed in individual environmental factor. However, in SA environment, complex environment is generated such as heat, pressure, and moisture, etc. Therefore, to assess the equipment survivability, type test under complex SA environment should be performed. Polymeric materials such as cable and valve seal for safety-related equipment are more vulnerable compared to metallic components in accident environment. [3]

Therefore, in this paper, the degradation behavior of nitrile butadiene rubber (NBR) exposed to a complex environment of post-accident condition was investigated. Degradation tests were performed in a simulated complex post-accident environment. To evaluate the degradation behavior of NBR, tensile and Shore A hardness properties were measured, and Fourier-transformed infrared (FT-IR) spectroscopy was used to investigate the change of molecular structure.

### 2. Materials and Methods

#### 2.1 Materials and degradation tests

The NBR with 28% acrylonitrile content samples were designed according to ISO37-2. temperature profile having a peak temperature of 627°C and a long-term ambient temperature of 187°C was evaluated based on simulations of various points in the containment building. [4] The degradation tests were performed under post-accident environment of a SA (heat, pressure, and chemical spraying condition). In the post-accident environment, a temperature of 187°C and pressure of 7.5 bar are maintained from 10 minutes to 24 hours after the initiation of accident. 4400 ppm boric acid solution was used to simulate the operation of the chemical spraying.

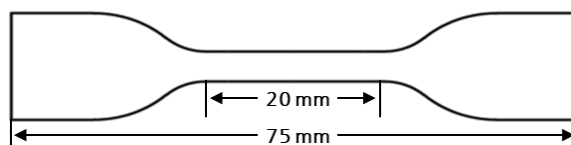


Fig. 1. Dimension of NBR sample (ISO37-2)

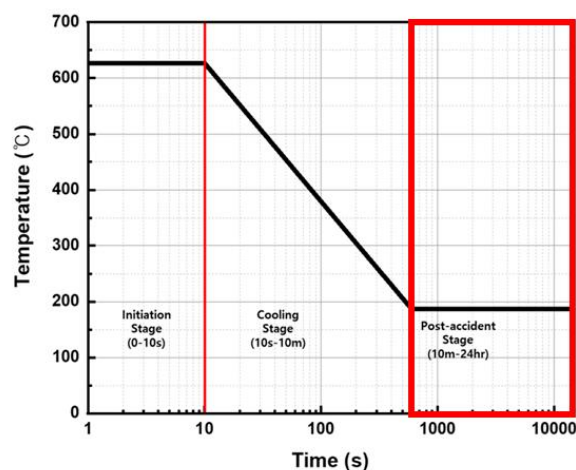


Fig. 2. Temperature profile of post-accident environment for equipment survivability

To evaluate the degradation in the post-accident environment, test matrix including 5 cases tests was

designed as shown in table I. In case 1, the test was performed by immersion in 4400 ppm boric acid solution at room temperature and pressure to investigate the effect of chemical spray solution and the test was conducted in the atmospheric air at 187°C using a furnace in case 2. In case 3, a test was performed at 30 bar so that boric acid solution could exist in the liquid at a temperature of 187°C using a closed loop system. The test conditions of case 4 were 187°C and 11.5 bar, in which boric acid was present in saturated steam, and in case 5, the test was performed at 187°C and 7.5 bar, and it existed inside the test section in the form of superheated steam.

Table I: Tests matrix under simulated post-accident environment

	Temperature	Pressure (bar)	Chemical
Case 1	25°C	-	Solution (4400 ppm B)
Case 2	187°C	-	Air
Case 3	187°C	30.0 bar	Solution (4400 ppm B)
Case 4	187°C	11.7 bar	Saturated steam (4400 ppm B)
Case 5	187°C	7.5 bar	Superheated Steam (4400 ppm B)

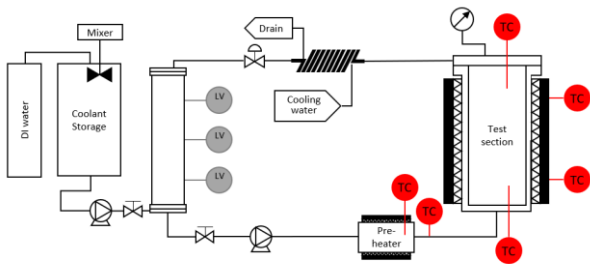


Fig. 3. Test facility for the degradation test

### 2.3 Characterization

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

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  $\text{cm}^{-1}$ , at a resolution of 4  $\text{cm}^{-1}$  and with an accumulation of four scans.

## 3. Results and discussion

### 3.1 Mechanical properties

In case 1, where the degradation test was performed at room temperature, the change in hardness was not significant, but in case 2~5 with test temperature of 187°C, the change in hardness was relatively large. In cases 2~5, oxygen was supplied, and degradation was accelerated to the auto-oxidation mechanism, resulting in a change in hardness of NBR. There is a difference in the amount of change in hardness in cases 2~5, which is caused by the supply and diffusion of oxygen in the environment of degradation test section. Solution or steam exist in the test section, and oxygen molecules in the air are prevented from diffusing and moving to the sample surface by  $\text{H}_2\text{O}$  molecules

As shown in table II, the amount of  $\text{H}_2\text{O}$  molecules in the test section was large in the order of case 3 – 4 – 5 – 2, and as mentioned above, assuming that  $\text{H}_2\text{O}$  molecules act as barrier the diffusion of oxygen, the amount of diffusing oxygen molecules to the sample surface is large in the order of case 2 – 5 – 4 – 3. As results of the measurement of hardness, the higher the amount of oxygen molecules diffusing to the sample surface, the higher the hardness, 89.75 in case 2 and 71.36, 76.3 and 82.96 in case 3, 4, and 5, respectively.

The EAB was measured to 791% of the reference case and was lowest the 15% in case 2 exposed to air, and 336, 295, and 225% in case 3, 4, and 5, respectively, as shown in Fig 5. The EAB was as low case 2 – 5 – 4 – 3 in the same order as the oxygen supply, and this trend is similar to the hardness measurement results. Oxygen supplied from the air causes crosslinking of NBR molecules to decrease the molecular activity to form a network structure, and this change of in molecular structure caused a decrease in EAB [5].

Table II: Mass of  $\text{H}_2\text{O}$  molecules in the test section

	Phase	Mass of $\text{H}_2\text{O}$ (1L test section)
Case 1	Liquid	Saturated
Case 2	-	-
Case 3	Liquid	877.310g
Case 4	Steam (Saturated)	6.002g
Case 5	Steam (Superheated)	3.706g

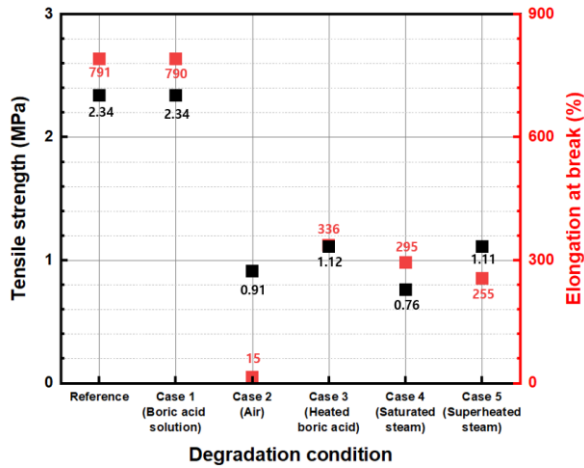


Fig. 5. Tensile properties (EAB and UTS) of NBR

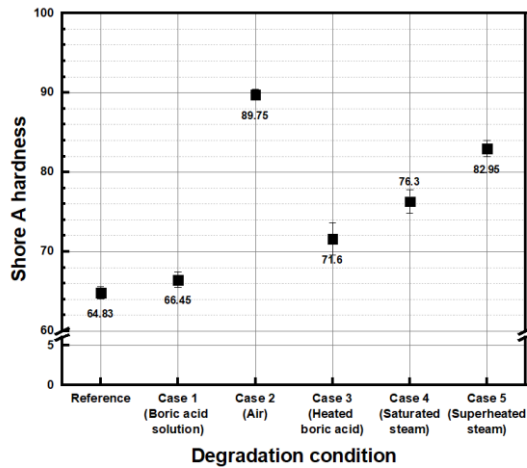


Fig. 4. Shore A hardness of NBR

### 3.2 Structural properties

As a results of molecular structure analysis using infrared spectroscopy, peak intensities of 988 and 1104  $\text{cm}^{-1}$  representing CH bonds and 1441  $\text{cm}^{-1}$  related to  $\text{CH}_2$  groups were decreased in NBR after case 2 to 5 tests. In cases 4 and 5, where the degradation tests were performed in steam, the peak intensity at 701 and 811  $\text{cm}^{-1}$  indicating C=C decreased. These changes of molecular structure were due to the cleavage of the CH and  $\text{CH}_2$  bonds as acceleration of the auto-oxidation reaction. The peak intensities of 2850 and 2918  $\text{cm}^{-1}$  related to the  $\text{CH}_2$  bonds were lower in the order of cases 2 – 5 – 4 – 3 as oxygen supply to sample surface, and the peak intensities of C-OH bond were also measured in the same trend. The  $\text{CH}_2$  bond decrease occurred to hydrogen generated from cleavage of chemical bond combined with OH to form  $\text{H}_2\text{O}$  molecules, which cause dehydration. Free radical group generated in cleavage reaction in the molecules combined with other molecules, free radical, and oxygen in the air to form a crosslinked structure as

increasing with the amount of oxygen supplied to sample surface.

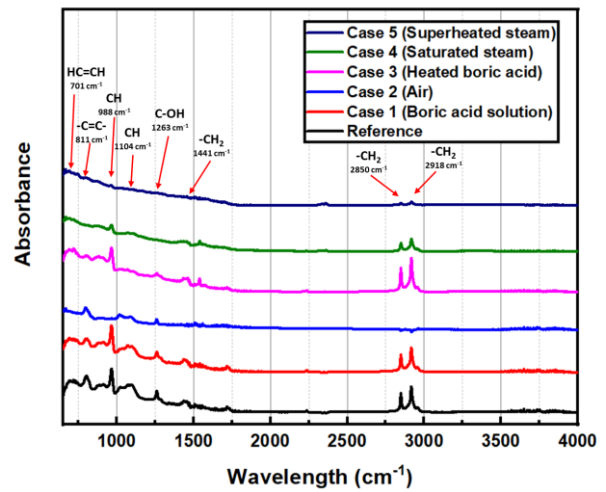


Fig. 5. FT-IR spectra of NBR

### 3. Conclusions

Degradation tests were conducted under simulated post-accident condition of SA environment and characterization of mechanical and structural properties to investigate the degradation behavior of NBR under simulated post-accident environment with various environmental factors. The auto-oxidation reaction occurs due to free radicals formed by cleavage of chemical bonds in SA environment and oxygen in the air, and is accelerated by supply of oxygen.

The NBR in case 1 tested under chemical spraying solution at a room temperature did not significantly affect the mechanical and structural properties. However, in case 2, most severe degraded in air, and in cases 3~5 where  $\text{H}_2\text{O}$  molecules were present in the test section, the smaller the oxygen molecules diffusing to sample surface as  $\text{H}_2\text{O}$  molecules amount. The oxygen molecules diffused to the sample surface affected the mechanical properties, and the cleavage of CH and  $\text{CH}_2$  in butadiene group in NBR was accelerated as the oxygen supply increased. Based on these results, in the SA complex environment,  $\text{H}_2\text{O}$  in the air act as a factor that inhibits the diffusion of oxygen to material surface, and also affects the mechanical and molecular structure. Therefore, it is recommended to design a type test for equipment survivability assessment in consideration of the synergistic effect between environmental factors in SA environment. [6]

### ACKNOWLEDGMENTS

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