Effects of steam and chemical spray solution on degradation of non-metallic materials

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1. Introduction

In nuclear power plants (NPPs), safety-related equipment is installed to maintain the integrity of the containment structure, main components, and systems, and to mitigate the impact of accidents during a design basis event (DBE). These safety-related equipment include non-metallic components such as seals, cable insulation or jackets, switches, and sensors. Nonmetallic components installed inside and outside safetyrelated equipment may be exposed to high-temperature steam and chemical spray solutions in a DBE environment. These environmental factors can cause the degradation of non-metallic materials, which can affect the safety function and reduce the lifetime of components and equipment. Non-metallic materials are widely used in various industries, including NPPs, due to their electrical insulation properties, chemical resistance, and mechanical elasticity. However, prolonged exposure to harsh environments can lead to mechanical and chemical property degradation. In particular, degradation caused by temperature and chemical exposure is one of the key factors that threaten the reliability of materials and equipment. Therefore, investigating the degradation behavior of non-metallic materials in extreme environments such as DBE conditions and evaluating their reliability and compatibility are essential to ensuring the integrity and safety of plant systems. The major factors that contribute to the degradation of non-metallic materials in a DBE environment include heat, radiation, pressure, steam, and chemical spray. Currently, NPPs follow the IEEE-323 standard and conduct a sequential equipment qualification (EQ) process. To meet the temperature and pressure profiles as well as chemical spray conditions of DBE environments, EQ tests are performed in chambers that simultaneously simulate these environmental conditions. However, evaluating the effects of environmental factors is challenging due to the complex synergistic interactions among multiple factors.

According to the IEC/IEEE- 60780-323, which was integrated in 2016, evaluations have been conducted not

only DBE performed in the EQ procedure but also on the applicability of EQ in design extension conditions (DEC), which has been internationally studied following the Fukushima accident. This evaluation has highlighted technical issues, including the effects of oxygen diffusion on the degradation behavior of materials and components. However, since an EQ procedure for DEC environments has not yet been fully established, its application in regulatory frameworks remain challenging. Additionally, there is insufficient research and data on the effect of oxygen diffusion on the degradation behavior of non-metallic materials, and studies on the quantification of these effects remain limited. As a result, these aspects have not yet been incorporated into current regulations. However, considering the increasingly stringent regulatory direction of NPP, these technical issues may be included in future regulations. Therefore, it is important to evaluate the effects of temperature, stem, and chemical spray on material degradation in DBE environments. Erica M. Redline et al. evaluated the effects of exposing ethylene-propylene diene rubber (EPDM) to various temperatures and atmospheric condition at 300°C, reporting that in the presence of steam, the degradation rate decreases due to factors such as oxidation rate, oxygen permeability, hydrolysis behavior, and peroxide formation mechanism. Seitaro Ito et al. also reported that the amount of degradation decreases due to effects of hydrolysis in in steam condition. However, previous studies have difference is testing condition to NPP, and data on degradation behavior for various materials remain limited. [1-3].

In this study, the degradation of nitrile butadiene rubber (NBR) was investigated under post-DEC condition for 24 hours, exposing, under various pressure, steam, and immersion conditions. After the aging tests, the evaluate the degradation behavior mechanical, thermal, and chemical properties were characterized.

2. Materials and Methods

In the degradation test, 28% acrylonitrile NBR was used, and specimens were designed in accordance with the ISO-37 type 2 standard for tensile testing. A total of 15 specimens were tested for each test case. To simulate the degradation under various condition of post DEC environment for 24 hours, degradation tests were conducted for a total of 5 test conditions, as shown in Fig. 1. Based on previous studies, at the post DEC temperature of 187°C, case 2 was tested in an atmospheric environment without steam, while case 3 was tested in an immersed condition with 30.0 bar abs. Case 4 and 5 were tested in steam environment at 11.7 and 7.5 bar abs, respectively. For immersion and steam test, a solution with a boron concentration 4400 ppm was used to simulate a chemical spray solution. As shown in Fig. 2, a testing loop was designed for the test case 3~5, and the specimens were placed in the autoclave test section.



Fig. 1. Saturation vapor pressure curve and test conditions



Fig. 2. Schematic diagram of testing loop for the degradation tests

To evaluate the degradation behavior, mechanical, thermal, and chemical properties were analyzed. For the assessment of mechanical properties, tensile tests were conducted in accordance with ASTM D412, using a crosshead speed of 50 mm/min, to measure elongation at break (EAB) and tensile strength (TS). Additionally, Shore A hardness was measured. For thermal properties,

thermogravimetric analysis (TGA) was performed to evaluate the weight change as a function of temperature. The test was conducted in the temperature range of room temperature to 900°C, with a heating rate of 10° C/min. To prevent oxidation during the test, nitrogen gas was purged. To assess the degradation of the chemical structure, Fourier-transform infrared (FT-IR) spectroscopy was used for spectrum analysis. The FT-IR analysis was conducted in attenuated total reflectance (ATR) mode using a Ge crystal plate, covering the wavelength range of 650–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3. Results and discussion

As shown in Fig. 3 and 4, there was no significant change of tensile properties between the reference (nondegraded condition) and case 1, where the specimens were immersed in a chemical spray solution at room temperature and atmospheric pressure. Similarly, shore A hardness did not significantly change between the reference and case 1. These results indicate that, under room temperature conditions, a 24 hours exposure to the chemical spray solution does not significantly contribute to the degradation of NBR. In case 2, the most significant degradation trend was observed. The EAB decreased from 791 to 15%, while the shore A hardness increased from 64.83 to 89.75, indicating severe hardening. This hardening phenomenon intensified in the order of case 3, case 4, and case 5. These results demonstrate that at 187°C, degradation in a steam environment is more severe than in an immersion condition with boric acid solution. Furthermore, the hardening effect was measured to be higher in the order of case 3, 4, and 5. Since case 4 contained a larger volume of steam in the test section compared to case 5, the formation of a moisture film on the specimen surface and the lower oxygen fraction in the atmosphere contributed to a slower acceleration of the autooxidation mechanism in case 4 than in case 5.



Fig. 3. Elongation at break (EAB) and tensile strength of degraded NBR



Fig. 4. Shore A hardness of degraded NBR

In Fig. 5, the FT-IR spectra after the degradation test were analyzed. The absorbance intensity of the CH bond (1104 cm⁻¹) and CH₂ bond (1441 cm⁻¹) decreased after the degradation test. It is considered that the thermal energy applied during the degradation test caused the cleavage of CH bonds, resulting in a decrease in absorbance intensity in the FT-IR spectrum. In case 4 and 5, where the tests were conducted in a steam environment, the absorbance intensity of the C=C bond 701, 811, and 960-970 cm⁻¹) decreased. This degradation behavior was similar to the behavior observed in mechanical properties and the hardening behavior, which can be attributed to molecular structural changes caused by the auto-oxidation mechanism. The degradation initiation site of NBR is known to be the C=C bond in the butadiene group. During the test, the thermal energy applied to the specimen cleaved the C=C bond, accelerating the degradation process. Therefore, the extent of degradation can be assessed based on the degradation intensity of the C=C bond. [4].

As shown in Fig. 6, the thermogravimetric curve was observed to behave differently depending on the test case. In particular, thermal degradation around 320°C shows a clear distinction between the cases. While the reference case and case 1 showed no significant difference, case 2, which was tested in atmospheric air at 187°C, exhibited a notable difference compared to the reference case. Furthermore, the discrepancy from the reference case was greater in case 3, 4, and 5, in that order. This trend is consistent with the hardening behavior observed in mechanical properties

The weight loss around 320°C during thermal degradation was analyzed to result from the volatilization of plasticizers such as dioctyl phthalate (DOP) and dioctyl terephthalate (DOTP), as shown in Fig. 7. Plasticizers, which have a polar portion, are added to decrease intermolecular forces and improve processability. However, as the plasticizers volatilize, the intermolecular forces increase, bringing molecules

into closer proximity. This accelerates crosslinking, as structures containing free radicals generated from the cleavage of chemical bonds due to thermal energy can form additional crosslinked structures. Consequently, these structural changes affect the bulk mechanical properties, ultimately leading to hardening. [5].



Fig. 5. FT-IR spectra of degraded NBR



Fig. 6. Thermogravimetric curve of degraded NBR



Fig. 7. thermogravimetric curve and 1st derivative weight curve of degraded NBR

4. Conclusion

In this study, the degradation behavior of NBR under air, steam, and chemical spray solutions in a post DEC environment was investigated. In case 1, the chemical spray solution at room temperature did not significantly affect the mechanical and structural properties. However, in case 2, where the test was conducted in air, the most severe degradation occurred. The degradation severity increased in the order of case 5, 4, and 3. The results show that auto-oxidation, the major degradation mechanism of NBR, occurred in the order of Case 2, 5, 4, and 3. The degree of degradation corresponded to the amount of oxygen available in the test section, with more oxygen access leading to more severe degradation. This trend indicates that oxygen diffusion to the specimen surface was inhibited by steam. Additionally, plasticizer volatilization followed a similar trend, contributing to the increase in crosslinking density.

As a result, the degradation trend shown in Fig. 8. was observed, and the hardening effect, represented by the increase in shore A hardness, was affected by the previously mentioned degradation factors.

For NBR to be used in nuclear power plants, it is essential to verify its survivability not only under normal operating conditions but also in DBE and DEC environments. To conduct such assessments, compatibility and component design should be performed based on data regarding the degradation behavior of NBR under various environmental conditions.

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Fig. 8. Normalized material properties of degraded NBR