Effect of Plasticizer Migration on Mechanical Properties of NBR under Thermal Aging

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1. Introduction

The polymeric material used as a sealing material for valves and actuators in nuclear power plants is exposed to heat during the long-term operation period. As a result, thermally aged polymeric materials can cause material degradation, which can affect the safety function of safety-related equipment. Currently, safety-related equipment in both normal operation and the design basis accident environment undergo an evaluation for operability through the equipment qualification process. However, the evaluation of the degradation level and characteristics in the component materials has not been sufficiently conducted [1]. Therefore, the degradation behavior of polymeric materials is necessary to ensure the safety of nuclear power plants. Plasticizers are added to polymeric materials to lower the glass transition temperature and increase processability, mechanical flexibility, ductility, and toughness. However, when the polymeric material is exposed to certain conditions, the plasticizer can cause diffusion and evaporation from the inside of the material to the surface or environment. This plasticizer migration can affect the mechanical properties of the material. Therefore, studies on plasticizer migration and mechanical properties are necessary to evaluate the integrity of polymeric materials under certain conditions [2].

In this study, the degradation behavior of nitrile butadiene rubber (NBR), which is used as a sealing material in nuclear power plants, under normal operating conditions was investigated. Accelerated thermal aging was performed to simulate the thermal aging that occurs during normal operation of nuclear power plants. To evaluate plasticizer migration, thermogravimetric analysis (TGA) and pyrolyzer gas chromatography/mass spectroscopy (Py-GC/MS) analysis were conducted, and hardness and tensile properties were measured. Fourier transformed-infrared (FT-IR) spectroscopy analysis was conducted to analyze the molecular structure because of thermal aging and plasticizer migration.

2. Materials and Methods

2.1 Accelerated Thermal Aging

The sulfur vulcanized NBR sheet with 28% acrylonitrile content were punched into dumbbell specimens according to the ISO 37- type 2, as shown in Fig. 1 [3].
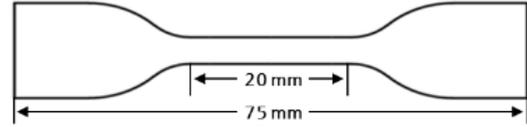
Fig. 1. Dimension of NBR sample (ISO37-2)

The accelerated thermal aging condition was determined by Arrhenius equation, maximum operating temperature, and operating period. Thermal decomposition activation energy was measured by thermogravimetric analysis according to ASTM E1641 using Flynn-Wall-Ozawa methods and TGA data in various heating rate as shown in equation (1) and Fig 2. The aging was conducted at 48.9 °C for 60 years to simulate the operating condition of 127.1 °C for 906.26 hours using activation energy (E_a) of 0.92 eV [4].

$$\ln(\beta) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \quad (1)$$

β: *Heating rate (K/min)*
A: *Pre-exponential factor (min^{-1})*
R: *Gas constant (J/mol K)*
T: *Temperature (K)*
E: *Activation energy (eV/mol)*
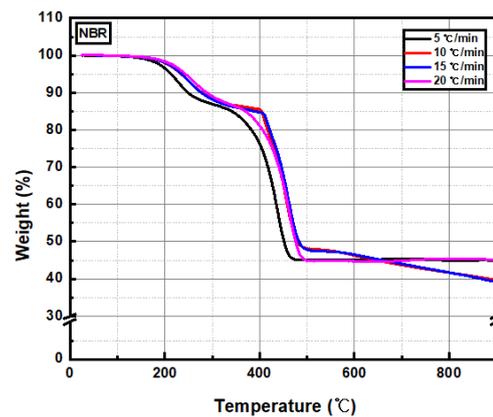
Fig. 2. Thermograms in various heating rate (5, 10, 15 and 20 °C/min) to measurement thermal decomposition activation energy of NBR.

Table I: Accelerated thermal aging condition

Activation Energy (E_a) (eV)	Operation Temperature (°C)	Operating Time (years)	Aging Temperature (°C)	Aging Time (hours)
0.92	48.90	60	127	906.26

2.2 Characterization

The mechanical properties were evaluated by conducting a tensile test and measuring the hardness. The elongation at break (EAB) and tensile strength (UTS) were determined according to ASTM D412 using type C specimens and a crosshead speed of 50 mm/min, with a self-tightening grip on an Instron 8801 machine. The durometer shore A hardness was measured following ASTM D2240. The FT-IR spectra were collected using a Nicolet iS50 FT-IR spectrometer equipped with a germanium attenuated total reflectance (ATR) attachment. The spectroscopic analysis was conducted over a wavelength range of 650 to 4000 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans accumulated. Thermograms were obtained using a thermogravimetric analyzer (TGA TA Q500) [5, 6].

The TGA was conducted in a nitrogen atmosphere with a heating rate of 10 ℃/min over a temperature range of 25 to 900 ℃. The powdered samples used for the TGA weighed around 5-10 mg. The crosslink density (V_e) was calculated using the equilibrium swelling theory (Flory-Rehner equation) and a 72-hour swelling test in toluene [7].

$$V_e = \frac{[ln(1-V_r)+V_r+\chi V_r^2]}{\left[\frac{V_1\left(V_r^{1/3}-V_r\right)}{2}\right]} \quad (2)$$

$$V_r = \frac{\frac{W_{dry}}{\rho_{dry}}}{\frac{W_{dry}}{\rho_{dry}}+\frac{W_{wet}-W_{dry}}{\rho_{solvent}}} \quad (3)$$

V_e: *Crosslink density (mol/cm³)*
V_r: *Volume fraction of polymer in swollen rubber*
χ: *Flory-Huggins polymer-solvent interaction parameter*
V_1:   *Molecular volume of solvent*
W_{dry}:   *Dry weight (g)*
ρ_{dry}:   *Dry density (g/cm³))*
W_{wet}:   *Weight after immersion test (g)*

3. Results and Discussion

3.1 Mechanical properties

The hardness and ultimate tensile strength (UTS) increased while the elongation at break (EAB) decreased with increasing simulated thermal aging time. This hardening phenomenon is due to the generation of free radicals from broken functional groups, which is accelerated by unstable structures that abstract hydrogen. Consequently, unstable molecules combine with other molecules, leading to crosslinking and the formation of a three-dimensional network. The thermodynamic incompatibility between stable and aged molecular structures results in weak links at their interface, which can affect the mechanical properties [8].
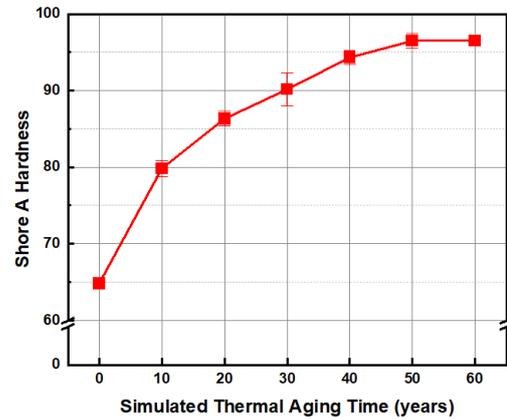
Fig. 3. Shore A hardness of accelerated thermal aged NBR
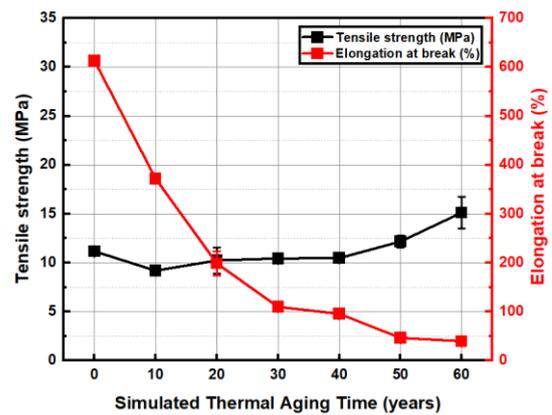
Fig. 4. Tensile strength (MPa) and elongation at break (%) of accelerated thermal aged NBR

3.2 Plasticizer Migration and Crosslinking Density

As shown in the thermogravimetric curve in Fig. 5, the 1st weight loss occurs at about 250 ℃. In polymeric material, weight loss occurs in thermogravimetric curve because functional groups cleaved from chemical bonds or additive in polymer system move out of the material in the form of gas. In order to identify the evolved gas, pristine NBR was heated to about 320 ℃, which is the temperature at which the first weight loss was completed, and gas analysis was conducted using Py-GC/MS. As a result of the analysis, dioctyl phthalate (DOP) and dioctyl terephthalate (DOTP) were identified. As shown in Fig. 7, when the weight loss of pristine NBR is used as a reference, the normalized weight loss due to simulated thermal aging increases gradually. This

indicates an increasing loss of plasticizer as aging time increasing.
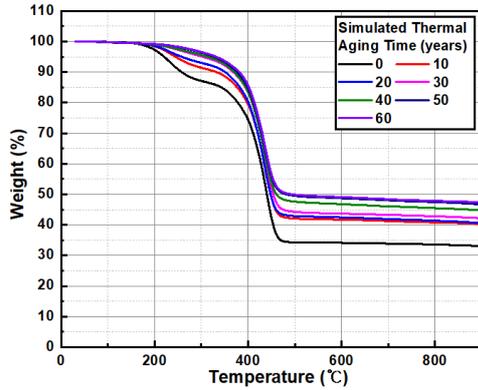
Fig. 5. Thermogravimetric curve of accelerated thermal aged NBR
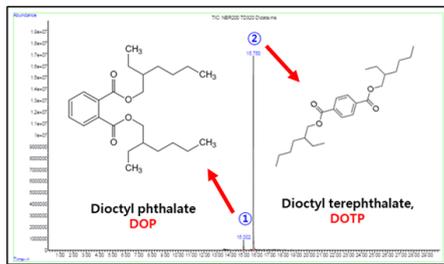
Fig. 6. Pyrolyzer-gas chromatography/mass spectrum of pristine NBR at 320 ℃
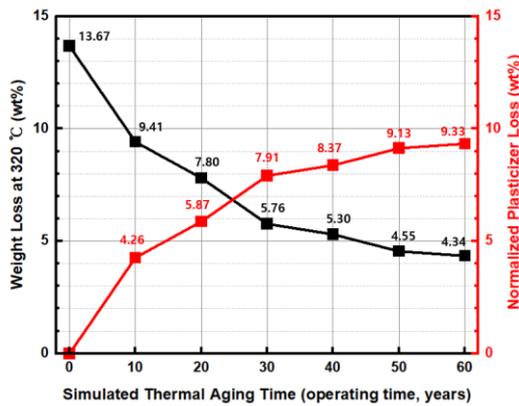
Fig. 7. Weight loss and normalized plasticizer loss of accelerated thermal aged NBR at 320 ℃

As shown in Figure 8, plasticizer loss and crosslinking density increased as the simulated thermal aging time increased. The mechanism of plasticization involves the formation of secondary bonds between plasticizer and polymer chains, where they act like "spacers," increasing the distance of neighbor chains, hindering their interaction and increasing their mobility. As the plasticizer content decreases, the dispersion force between polymer chains and their interactions increase, leading to an increase in crosslinking. In addition, free

radicals or unsaturated bonds generated by thermal oxidative degradation reactions during accelerated thermal aging can accelerate the increase the crosslinking [9, 10].
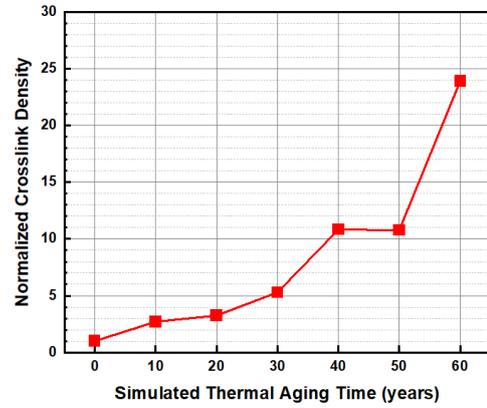
Fig. 8. Crosslink density of accelerated thermal aged NBR

3.1 Structure analysis

The infrared absorption spectra for the NBR are shown in Fig. 9. The broad absorbance peaks of 2918 and 2848 cm^{-1} are attributed to stretching vibration of $-CH_2$, and the absorption at 2235 and 1267 cm^{-1} corresponds to the stretching vibration of $-C\equiv N$ in the acrylonitrile and $-C-N$. The absorption at 1726 and 1436 cm-1 indicate to CH_2 deformation due to C=O and C=O. C=C in butadiene group (918, 964 cm^{-1}). The strong peak around 1000 cm^{-1} is from silica, one of the reinforcing fillers in NBR. It stayed unchanged because silica is stable during thermal aging, although its intensities seemed to change because more silica particles were exposed to the surface with the thermal degradation of the NBR matrix. The peaks at 1015-1117 and 1533 cm^{-1} attributed to additives. The peaks at 918 and 964 cm^{-1} correspond to C=C in butadiene group [11, 12].
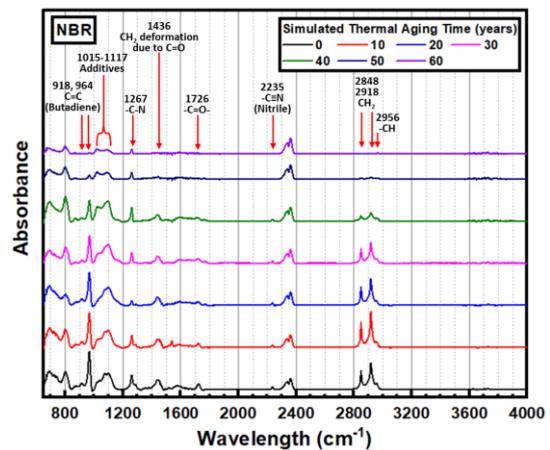
Fig. 9. FT-IR spectra of accelerated thermal aged NBR

3. Conclusion

To investigate the effects of thermal aging during the normal operation period on the degradation of NBR, the tensile properties and Shore A hardness were measured, and the molecular structure was analyzed through TGA and FT-IR spectroscopy. As the duration of accelerated aging increased, the EAB decreased, and the hardness increased, indicating a hardening phenomenon in the NBR. TGA analysis showed that the weight loss decreased around 250 ℃ as the duration of accelerated aging increased. Weight loss is caused by the evaporation of elements from the material, and as the duration of accelerated aging increases, the weight loss due to evaporation on the TGA curve decreases. The Py-GC/MS analysis identified the volatile substance as plasticizers, such as DOP and DOTP. The effects of thermal aging on plasticizer migration and hardening increase with increasing duration of accelerated aging. The evaporation of plasticizers, which weaken intermolecular forces, leads to a decrease in the distance between molecules and an increase in attractive forces. In addition, oxidative degradation caused cleavage of chemical bonds, leading to an increase in crosslink sites. Consequently, the increase in crosslinking sites due to oxidative degradation and the increase in intermolecular forces caused by plasticizer loss both lead to an increase in crosslink density, affecting the mechanical properties of NBR.

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