

# Reliability and Thermal Aging of Polymers Intended to Severe Operating Conditions <sup>†</sup>

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**Abstract:** The objective of this work is the development of a methodology to determine the useful life based on the storage temperature of NBR O-rings using a reliability-based approach that allows one to predict the use suitability at different supposed storage scenarios (that involve different storage time and temperature) considering the further required in-service performance. Thus, experimental measurements of Shore A hardness have been correlated with storage variables. From the study, it has been verified that for any of the analysis scenarios, the limit established criterion is above the storage time premise considered in the usual nuclear industry practices.

**Keywords:** reliability; prognostics; design-for-reliability; aging; elastomers; durability; harsh environments

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## 1. Introduction

The determination of mechanical properties of materials provides the basis for the fundamental understanding of the behavior of components that can experience degradation in operation and/or even during storage. A very representative example is the thermal aging mechanism that severely affects materials that are ultimately intended to operate in a harsh operating environment as that of a nuclear reactor. Reliability evaluation plays an important role in the design and development of any engineering system [1]; thus, some studies [2,3] have correlated main polymer properties with final performance and durability.

Polymers, and especially elastomers, play a key role as part of the many mechanical, electrical, and electronic components found in nuclear power generation plants. The degradation of polymeric materials is a frequent phenomenon that is accelerated, in many cases, by arduous operating conditions. Elastomers, especially rubbers—such as acrylonitrile butadiene, NBR—experience degradation that is favored by contact with oxygen [4]. This type of reaction, which triggers the irreversible damage of the component, is also favored by an increase in the operating temperature. Therefore, it is of interest to analyze how their intrinsic properties influence their thermal aging.

One of the most usual parts with relevant safety-related functions in nuclear equipment is the NBR O-rings or gaskets that are used as mechanical sealing elements, since their safety function is being capable of preventing any leakage (whether internal or external) throughout the useful life of the equipment [5]. The objective of this work is the

development of a methodology to determine the useful life based on the storage temperature of NBR O-rings using a reliability-based approach that allows one to obtain the health condition at different supposed storage scenarios, considering the required in-service performance.

For the study, NBR was selected as a gasket material, since a previous work [3] has shown that acrylonitrile is the best option to withstand moderate levels of radiation thresholds extracted from databases [6,7] as well as its recyclability, providing a sustainable life cycle. The evaluated parameter was the Shore A hardness in accordance with ISO 868 [8] during a period of five years. The thermal hardening was quantified based on an adaptation of the Arrhenius model-based correlation between hardness and temperature and storage time. The study incorporates a comparison between the results obtained for newly manufactured and existing O-rings in the warehouse, considering several statistical scenarios.

## 2. Methodology

The methodology is based on the analysis of experimental data of Shore A hardness obtained during qualification processes (between 2014 and 2018) of newly manufactured and previously-stored NBR O-Rings. Thus, by adapting the Arrhenius model (Equation (1)) for thermal aging along with the activation energies indicated in the standard EPRI TR 1009748 [9], predictions based on three scenarios were considered: very conservative, moderately conservative, and minimally conservative.

$$t_s = t_a \cdot \exp \left[ \frac{E_a}{k} \left( \left( \frac{1}{T_a} \right) - \left( \frac{1}{T_s} \right) \right) \right] \tag{1}$$

where:

$t_s$ : Estimated lifetime in service (hours)

$t_a$ : Time considering acceleration in aging/degradation (hours)

$T_s$ : Normal operating temperature (K)

$T_a$ : Hardening temperature (K)

$E_a$ : Activation energy (eV)

$K$ : Boltzmann constant =  $0.8617 \cdot 10^4$  eV/K

Table 1 shows the mean value of more than 140 Shore A hardness measurements made during the period between 2014 and 2018. Likewise, the study incorporated 12 hardness tests on stored O-rings without a defined date. Nevertheless, it is known that they were entered into inventory in 2000 and that they could be dated as much from 1994.

**Table 1.** Experimental data analyzed in this work <sup>1</sup>.

Supply Description	Shore A Hardness (Mean Value)
New supplies (acquired between 2014 and 2018)	61.33
Supplies in storage for at least 18 years	69.78
Evaluation Parameter	Hardening (%)
Comparison new to storage supplies	13.81

Note: <sup>1</sup> Storage conditions:  $20 \pm 5$  °C; relative humidity: 50–60%.

Considering the uncertainty about the date of manufacture of the previously-stored O-rings, three scenarios were defined for the analysis: very conservative, moderately conservative, and minimally conservative. Subsequently, for the conservative interval, it was considered that the age of the O-rings was 24 years, for the middle one (moderately conservative) it was 22.5 years, and for the least conservative one, 18 years (calculated on the test date in 2018).

Using an adaptation of the Arrhenius model, predictions based on hardness results can be made over a five-year period, including supplies stored for at least 18 years. Once

the calculation model was proposed, different storage limit conditions were obtained after validating the methodology comparing the predicted allowable storage periods and conditions with the real ones.

### 3. Results

Table 2 shows the maximum temperature obtained using (Equation (1)) and the calculation parameters indicated in Note <sup>2</sup> (at the bottom of the Table).

**Table 2.** Prediction of the maximum allowable storage temperature according to the Arrhenius model <sup>2</sup>.

Maximum Allowable Storage Temperature (°C)		
Very Conservative (24 Years)	Moderately Conservative (22 Years)	Minimally Conservative (18 Years)
27.5	26.31	25.17

Note: <sup>2</sup> The following parameters have been used for the calculation: normal operating temperature ( $T_s$ ) = 33 °C; operation time = 10 years; activation energy ( $E_a$ ) according to EPRI TR 1009748 for NBR = 0.88 [9].

In view of the results presented in Table 2, it can be concluded that the limit conditions for prolonged storage considering any of the three contemplated scenarios would be above the real conditions. That is, even in the case of the least conservative scenario, the maximum temperature predicted by the model is 25.17 °C, which is slightly higher than the maximum real temperature (according to Note <sup>1</sup>—Table 1 = 20 ± 5 °C).

On the other hand, a validation (Table 3) was performed to check if in the analyzed assumptions, (18, 22.5, and 24 years) the maximum allowable hardness value according to the catalog would be reached for these NBR gaskets, that is, a value of 70 Shore A.

**Table 3.** Results of the application of the Arrhenius-based model and validation.

Analysis Scenario	Time (Years) to Reach the Maximum Allowable Hardness (70 Shore A)
Minimally conservative	18.35
Moderately conservative	22.93
Very conservative	24.46

Adapting the model to predict for each of the three scenarios in which the maximum allowable hardness value (70 Shore A), defined as the upper limit, would be reached, it is verified that for any of the scenarios the upper limit value is above the considered storage time premise (18.35 > 18 years considered for the least conservative scenario, 22.93 > 22.5 years considered for the medium scenario, and 24.46 > 24 years considered for the most conservative scenario). Therefore, it is possible to validate the model, by ensuring that in the predictions (both for temperature ranges and for storage times) the allowable limit value of 70 Shore A is not reached in any case.

### 4. Conclusions and Future Works

A degradation model was obtained, as a function of storage time and temperature. As a case study, NBR O-rings for nuclear applications were considered. Using this analytical methodology, predictions based on hardness results were made over a five-year period, including supplies stored for at least 18 years. Once the calculation model was proposed, different storage limit conditions are obtained. In addition, a validation of the methodology was performed by comparing the predicted allowable storage periods and conditions with the real ones.

Thus, it was verified that for any of the scenarios, the upper limit value is above the considered storage time premise (18.35 > 18 years considered for the least conservative scenario, 22.93 > 22.5 years considered for the medium scenario, and 24.46 > 24 years considered for the most conservative scenario). Therefore, it is possible to validate the model, by ensuring that in the predictions (both for temperature ranges and for storage times) the allowable limit value of 70 Shore A is not reached in any case.

Finally, it was proven that the storage strategies of our nuclear power plants are successful, perfectly meeting the expectations of suitability and functionality of the components when they are installed after storage. This methodology can be used in the future to analyze materials suitability after a long storage period.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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