

Reliability and Thermal Aging of Polymers Intended to Severe Operating Conditions [†]

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† Presented at the First International Conference on “Green” Polymer Materials 2020, 5–25 November 2020; Available online: <https://cgpm2020.sciforum.net/>.

Published: 4 November 2020

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 to predict the use suitability at different supposed storage scenarios (that involves 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 of the storage time premise considered in the usual nuclear industry practices.

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

1. Introduction

The determination of mechanical properties of materials provides the basis for the fundamental understanding of the behaviour 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 polymers 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 favoured by contact with oxygen [4]. This type of reaction -which triggers the irreversible damage of the component- is also favoured by an increase in the operating temperature. Therefore, it is of interest to analyse how their intrinsic properties influence their thermal aging.

One of most usual parts with relevant safety-related function 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 to obtain the health condition at different supposed storage scenarios, considering the required in-service performance.

For the study, NBR has been selected as a gasket material, since a previous work [6] has shown that acrylonitrile is the best option to withstand moderate levels of radiation thresholds extracted from databases [7,8] as well as its recyclability, providing a sustainable life cycle. The evaluated parameter has been the Shore A hardness in accordance with ISO 868 [9] during a period of five years. The thermal hardening is quantified based on an adaptation of 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 2019) 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 [10]-predictions based on three scenarios are 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 2019. Likewise, the study has incorporated 12 hardness tests on stored O-rings without a defined date. Nevertheless, it is known that they were entered into inventory in 1998 and that they could be dated as much from 1992.

Table 1. Experimental data analyzed in this work ¹.

Supply Description	Shore A Hardness (Mean Value)
New supplies (acquired between 2014 and 2019)	61.33
Supplies stored at least 18 years	69.78
Evaluation Parameter	Hardening (%)
Comparison new to storage supplies	13.81

Note *1: Storage conditions: 20 ± 5 °C; relative humidity: 50–60%.

Considering the uncertainty about the date of manufacture of the previously stored O-rings, three scenarios have been defined for the analysis: very conservative, moderately conservative and minimally conservative. Subsequently, for the conservative interval, it has been considered that the age of O-rings was 24 years, for the middle one (moderately conservative) was 22.5 years and for the least conservative one, 18 years old (calculated on the test date in 2016).

Using an adaptation of the Arrhenius model, predictions based on hardness results can be made over the 5-year period, including supplies stored for at least 18 years. Once the calculation model has been proposed, different storage limit conditions are 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 *2 (at the bottom of the Table).

Table 2. Prediction of the maximum allowable storage temperature according to the Arrhenius model.

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

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

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 *1—Table 1 = 20 ± 5 °C).

On the other hand, a validation (Table 3) is 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 in 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 of 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 has been obtained, as a function of storage time and temperature. As a case study, NBR O-rings for nuclear applications has been considered. Using this analytical methodology, predictions based on hardness results have been made over a 5-year period, including supplies stored for at least 18 years. Once the calculation model has been proposed, different storage limit conditions are obtained. In addition, a validation of the methodology has been performed by comparing the predicted allowable storage periods and conditions with the real ones.

Thus, it has been 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 has been 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.

Author Contributions: Conceptualization, A.R.-P., M.C. and A.M.C.; Formal analysis, A.R.-P., E.P. and A.M.C.; Funding acquisition, A.R.-P., M.C. and A.M.C.; Investigation, A.R.-P. and E.P.; Methodology, A.R.-P. and A.M.C.; Project administration, A.R.-P.; Resources, A.R.-P., E.P. and A.M.C.; Supervision, A.R.-P. and A.M.C.; Validation, A.R.-P., M.C. and A.M.C.; Writing—original draft, A.R.-P.; Writing—review & editing, A.R.-P., E.P. and A.M.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work is part of the activities included in the transfer contract of research results with reference 2019-CTINV-0068 (based on Article 83 of the Spanish Universities Act, 2007) between UNED and SGS TECNOS, being the scope aligned with the 9th Sustainable Development Goal related to “Industry, Innovation and Infrastructure”, as established by United Nations and included by the Spanish Government in the “Agenda 2030”. In addition, this work has also been partially funded by the Annual Grants Call of the E.T.S.I. Industriales of UNED through the projects of references 2020-ICF04/B and 2020-ICF04/D.

Acknowledgments: The authors want to thank Prof. Frigione (University of Salento) for her kind invitation to participate with this contribution in the session on “Durability & Aging, Degradation & Biodegradation” of the CGPM 2020. The authors also want to thank Blas Galván (ULPGC) for his high valuable conceptual contributions. In addition, Ernesto Primera wants to thank the University of Delaware’s StatLab and, specially, Fan (Assistant Professor of Reliability and Survival analysis). This work has been realized in the framework of the activities of the Research Group of the UNED “Industrial Production and Manufacturing Engineering (IPME)” and the Industrial Research Group “Advanced Failure Prognosis for Engineering Applications”.

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

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