

# Investigation of Long-Term Behaviour of Elastomeric Seals for Transport and Storage Packages

A. Kömmling, D. Wolff and M. Jaunich

**Abstract** Elastomers are widely used as the main sealing materials in containers for low- and intermediate-level radioactive waste and as an additional component for metal seals in spent-fuel and high-level waste containers. According to appropriate guidelines and regulations, safe enclosure of the radioactive container contents has to be guaranteed for lengthy storage periods of at least 40 years. Therefore, the understanding of seal ageing behaviour is of high importance and has to be considered with regard to possible dynamic events taking place during transport after storage. An accelerated ageing approach for compressed seals is presented, as well as some first results.

## 1 Introduction

Elastomers are widely used as main sealing materials in containers for low- and intermediate-level radioactive waste and as an additional component for metal seals in spent-fuel and high-level waste containers. This requires a service life in the range of several decades. According to appropriate guidelines and regulations, safe enclosure of the radioactive inventory has to be guaranteed for lengthy storage periods, as well as down to temperatures of  $-40\text{ }^{\circ}\text{C}$  for transportation. Therefore, the understanding of seal behaviour in general is of high importance, and especially ageing of elastomeric seals has to be considered. Possible dynamic loads may occur during the whole interim storage period (so far approved in Germany for up to 40 years) and during transportation after storage. To fulfil their purpose, the seals have to remain in good shape with adequate resilience to ensure a certain contact pressure and without, e.g. cracks crossing the sealing surface that would act as leakage paths.

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Ageing of materials is an undesirable, but unavoidable, process that can lead to (non-reversible) changes in, e.g. mechanical properties, thermal properties, colour and chemical composition [1]. The origin of these property changes can be innate to the material or caused by influences from the environment. Typical innate effects are, e.g. trapped stresses or remaining crosslinking agents. Effects caused by the environment are, e.g. oxidation processes, influences from light and other radiation sources and heat.

The changes of the material properties can be caused by purely physical or chemical processes. Physical ageing can take place as molecular rearrangement, demixing or crystal growth. Usually it is driven by thermodynamic non-equilibrium conditions, which are often innate effects. Chemical ageing results in changes of the chemical composition of the material by chemical reactions. Ageing of polymeric materials is generally considered to consist of two pathways. One is the formation of additional crosslinks, and the other is chain scission [2]. Generally, these two processes take place in parallel while one process is dominant. This means that some materials primarily tend to crosslinking and others to chain scission. The predominant mechanism can change over the whole ageing period. Additionally, temperature has an important influence on the ageing process. It is possible that a material forms a high amount of crosslinks at one temperature and at, e.g. that, at a higher temperature, chain scission becomes dominant.

To describe the effect of ageing on the performance of a material, it is important to test the relevant properties. For long-term applications, an accelerated test is required to ensure long-term safety. This approach is described by standards, e.g. ISO 188 [3]. Often these standards address only the general approach for accelerated ageing and assume an Arrhenius-like behaviour of the ageing process, whereas the necessary prerequisites and the data analysis are often not described in detail. Moreover, often these standards describe ageing of standard samples and not of components. The samples are often unstressed and therefore the effect of a continuous deformation of, e.g. an elastomeric seal cannot be evaluated even if such permanent stress might lead to different ageing effects as, e.g. predominantly chain scission of stressed chain molecules.

In the literature, there are several examples that show non-Arrhenius ageing effects and, therefore, the need for a more detailed analysis of the test results and a careful selection of test parameters [4, 5]. Especially the interactions in complex technical elastomer compounds consisting of a multitude of different components are hard to predict.

As some material properties are more sensitive to changes during ageing than others, it is important to measure a range of various properties, e.g. chemical, mechanical and thermal properties. However, some measured properties, such as tear strength, have typically very little or a highly complex correlation with sealing performance [6]. Other standard methods such as compression set or stress relaxation measurement are more related to seal applications, providing an indirect value for seal performance [5]. An overall goal of ageing investigation of seal materials is to determine which properties are sensitive to occurring changes and how they are correlated with the safety-relevant performance of the seal.

Our previous work was concerned mainly with the low-temperature behaviour of elastomeric seals and modified compression set tests [6–9].

In this paper, we focus on our approach to investigate the behaviour of elastomeric seals over extended periods of time at elevated temperatures. We describe our approach to investigate the occurring changes of material properties of elastomeric seals by ageing performed at various temperatures and under assembly conditions. First results are presented as well. One goal is to determine the influence of compression during the ageing period, and therefore compressed and uncompressed samples are aged and compared. The temperature influence must also be analysed to ensure an appropriate acceleration of the ageing processes (e.g. exclusion of additional sample degradation as a result of high ageing temperatures).

## 2 Material Selection and Ageing Conditions

As mentioned, the use of elastomeric seals in containers for radioactive waste is our motivation to start the described research, and, hence, the investigation parameters and the material selection are related to this application.

The material selection focuses on material classes that are internationally used for this application. Therefore, a fluorocarbon rubber (FKM) and an ethylene-propylene-diene rubber (EPDM) were selected. Additionally hydrated nitrile butadiene rubber (HNBR) was tested for comparison.

The seal dimensions were chosen with a rather high torus diameter of 10 mm and an inner diameter of 190 mm to have a sufficient amount of sample material for the various analytical methods to be performed. Mechanical ageing conditions should also be varied to investigate whether a compressed seal shows a different ageing behaviour in comparison to an uncompressed sample.

Ageing temperatures are selected in the range from 75 °C up to 150 °C and are therefore spread broad enough to have a significant acceleration. With a total of four test temperatures, a sufficient amount of data should be available to judge the applicability of typical time-temperature-superposition approaches as, e.g. the Williams-Landel-Ferry approach combined with the Arrhenius approach.

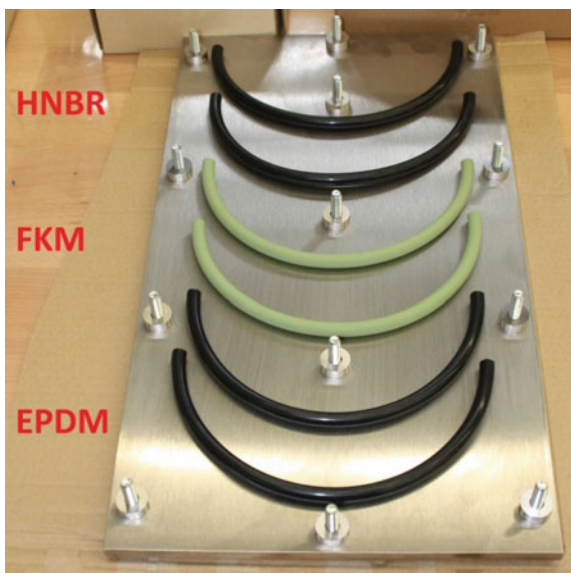
During ageing, samples are stored in unstressed condition as complete O-rings and in compressed condition with a degree of compression of 25%. To compress the seals, they are positioned between two metal plates that are screwed together until both plates are pressed against distant pieces. The devices used are schematically shown in Figs. 1 and 2.

Besides these two ageing conditions, it is important to allow a correlation of measured changes in material properties with seal function, which is possible with seals mounted in flanges. These flanges are pictured in Fig. 3. This setup enables leakage-rate measurements of mounted seals by a pressure-rise measurement after

**Fig. 1** Uncompressed O-rings ageing on racks of punched sheets

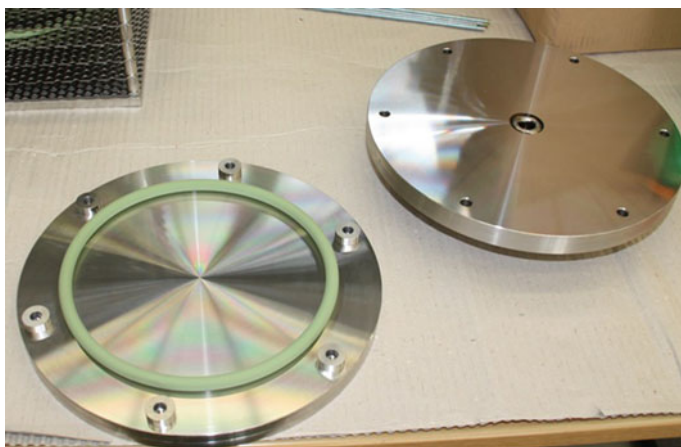


**Fig. 2** O-rings ageing in compression between plates



predefined ageing times. The principle setup for such a measurement is described in [6, 10].

The samples are removed from the high-temperature chamber at predefined times to be investigated by several methods. The ageing times are given in Table 1.



**Fig. 3** Test flanges for leakage/rate measurements

**Table 1** Ageing times and number of O-rings for the various ageing setups

| Storage time         | 0 h | 3 h | 10 h | 1 d | 3 d | 10 d | 30 d | 100 d | 0.5a | 1a | 2a |
|----------------------|-----|-----|------|-----|-----|------|------|-------|------|----|----|
| Uncompressed samples | 3   | 1   | 1    | 1   | 1   | 1    | 1    | 1     | 1    | 1  | 1  |
| Compressed samples   |     | 1   | 1    | 1   | 1   | 1    | 1    | 1     | 1    | 1  | 1  |
| Samples in flange    | 3   |     |      |     |     |      |      |       |      |    |    |

### 3 Analytical Methods

For the investigation of ageing effects, several methods are helpful to describe the occurring changes and to quantify the influence on the seal performance. For the investigation of structural/morphological changes, suitable methods are, e.g.

- FT-IR infrared spectroscopy for detecting changes in the chemical structure, e.g. crosslinking or insertion of oxygen (oxidation)
- Differential Scanning Calorimetry (DSC) for detecting phase transitions over temperature
- Thermal Gravimetric Analysis (TGA) for measuring the mass loss of a sample during a heating programme as a result of decomposition processes.

For investigation of mechanical properties, several methods can be applied, such as

- Dynamic Mechanical Analysis (DMA) for measuring the modulus in dependence of temperature to characterise the viscoelastic properties of the material and occurring transitions
- Compression Set (CS) as a seal-related property that measures the recovery behaviour after compression at various temperatures

- Compression stress relaxation as a measure of sealing-force decay
- Hardness
- Tensile testing.

The observed changes shall be correlated with the leakage rate of the aged seals.

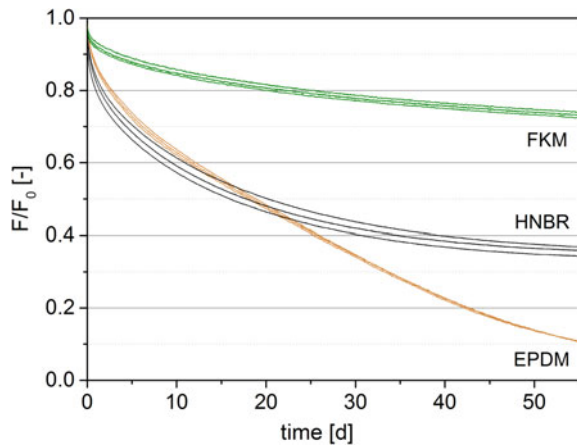
## 4 First Results and Discussion

Results of compression stress relaxation experiments of the elastomers are shown in Fig. 4 where the decrease of sealing force  $F$  is normalized to the initial force  $F_0$ . Three samples of each material were tested at 150 °C [11,12].

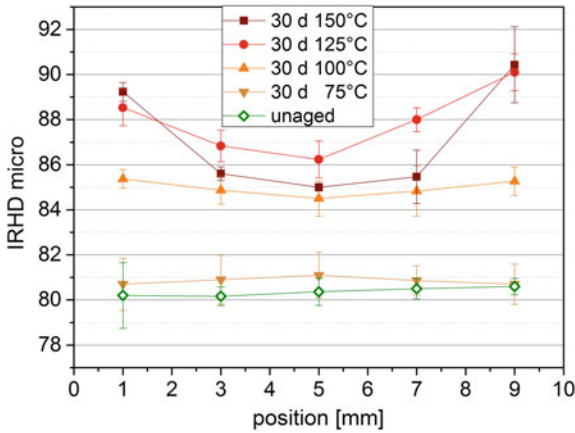
After the initial fast drop within the 1 h of the experiment, the materials show a distinct behaviour. FKM shows the slowest decrease with time. HNBR decreases fast within the first days, but the decrease rate becomes smaller and the compression force of EPDM continues to decrease rapidly. This is probably due to diffusion-limited oxidation (DLO) effects [13, 11] which can appear in thick samples at high ageing temperatures. Then, the ageing reactions are so that fast on the outer sample side, which is exposed to air containing oxygen, that it consumes most of the oxygen or forms an oxygen-diffusion barrier through crosslinking reactions (indicated by an increase in hardness). Thus, the inner part of the sample is protected from oxidation and can retain its elastic properties. As the micro hardness measured across the O-ring cross-section (shown in Figs. 5 and 6) indicates, these heterogeneous ageing effects occur in HNBR after 30 d at 150 °C, but not in EPDM. Thus, EPDM degrades across the whole sample, while HNBR can retain an elastic core.

Results of hardness measurements on the sealing area of HNBR seals are shown in Figs. 7 (uncompressed) and 8 (compressed). The uncompressed samples show a

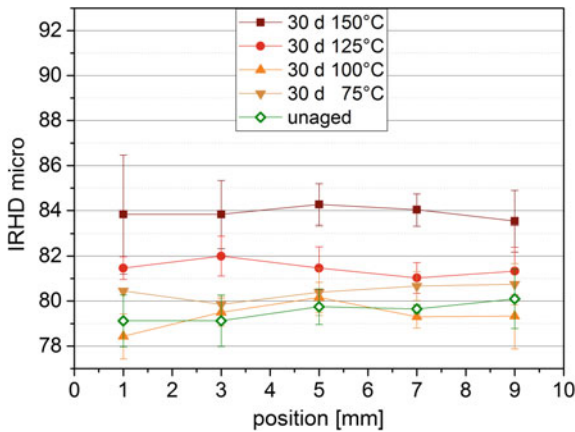
**Fig. 4** Decrease of normalized sealing force vs. time at 150 °C



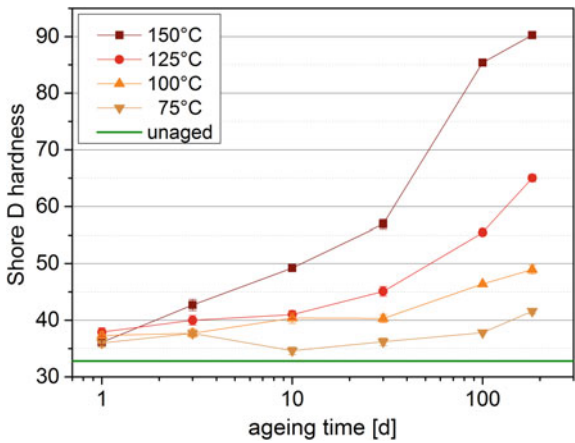
**Fig. 5** Micro hardness profiles across HNBR seals (Ø 10 mm) aged for 30 d



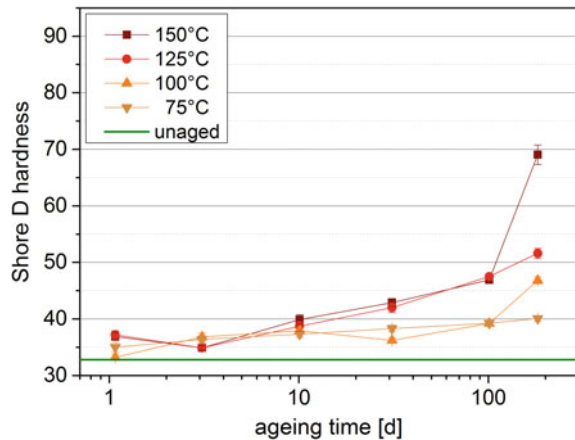
**Fig. 6** Micro hardness profiles across EPDM seals (Ø 10 mm) aged for 30 d



**Fig. 7** Hardness measured on the sealing area of uncompressed HNBR seals



**Fig. 8** Hardness measured on the sealing area of compressed HNBR gaskets



higher hardness increase compared to the compressed samples. This is because the sealing area of the compressed seal is covered by flanges. Thus, oxygen access is hindered for this sample arrangement and ageing is slowed. This illustrates that the reduced area for oxygen access has to be taken into account for seals aged in compression.

## 5 Conclusion

The investigation of the ageing behaviour of elastomeric seals is an important factor for the assessment of the long-term performance of sealed containers.

Ageing is a complex process that involves multiple reactions. To describe the material behaviour in the necessary extent, an in-depth understanding of these reactions and their influence on the sealing function is necessary. As standard procedures of polymer ageing are typically designed for the lifetime estimation for goods having much shorter service lives, those standard regulations seem not well-fitted for the lifetime estimation over several decades. Therefore, we propose and perform ageing experiments tailored to the particular needs for elastomeric-seal evaluation with the focus on application for a lifetime of several decades. First results have shown that the access of oxygen plays an important role in the degradation, which is influenced both by the dimensions of the sample (thickness) and by the compression assembly (covering by flanges).

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## References

1. DIN 50035:2012–09, Begriffe auf dem Gebiet der Alterung von Materialien—Polymere Werkstoffe
2. Ehrenstein GW, Pongratz S (2007) Beständigkeit von Kunststoffen, vol 1. Carl Hanser Verlag, München
3. ISO 188:2011, Rubber, vulcanized or thermoplastic- Accelerated ageing and heat resistance tests
4. Celina M, Gillen KT, Assink RA (2005) Accelerated aging and lifetime prediction: review of non-Arrhenius behaviour due to two competing processes. *Polym Degrad Stab* 90:395–404
5. Marlier R, Andre R, Malesys P, Issard H (2006) Seal life of EPDM O-rings at high temperature determined by unique method. *Packag Trans Storage Secur Radioact Mater* 17:57–62
6. Jaunich M (2012) Tieftemperaturverhalten von Elastomeren im Dichtungseinsatz. Doktorarbeit an der Bundesanstalt für Materialforschung und Prüfung, Berlin
7. Jaunich M, Stark W, Wolff D (2010) A new method to evaluate the low temperature function of rubber sealing materials. *Polym Test* 29:815–823
8. Jaunich M, Stark W, Wolff D (2012) Comparison of low temperature properties of different elastomer materials investigated by a new method for compression set measurement. *Polym Test* 31:987–992
9. Jaunich M, Wolff D, Stark W (2013) Low temperature properties of rubber seals—results of component tests. *KGK-Kautsch. Gummi Kunstst* 66:26–30
10. Jaunich M, von der Ehe K, Wolff D, Völzke H, Stark W (2011) Understanding low temperature properties of elastomer seals. *Packag Trans Storage Secur Radioact Mater (RAMTRANS)* 22:83–88 (2011)
11. Kömmling A, Jaunich M, Wolff D (2016) Effects of heterogeneous aging in compressed HNBR and EPDM O-ring seals. *Polym Degrad Stab* 126:39–46
12. Kömmling A, Jaunich M, Wolff D (2016) Ageing of HNBR, EPDM and FKM O-rings, *KGK* 69(4):36
13. Wise J, Gillen KT, Clough RL (1997) Quantitative model for the time development of diffusion-limited oxidation profiles. *Polymer* 38:1929–1944

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