Ageing of HNBR, EPDM and FKM O-rings

Introduction
Elastomers are widely used as sealing materials due to their excellent elastic properties and relatively low cost. However, their use has its limits, e.g. at low temperatures [1-3] or for very long time periods due to chemical ageing of the material. With ageing, the elastomers can gradually lose their elasticity and their ability for recovery [4], which might result in a leakage rate above the specified level. Some applications, e.g. in containers for radioactive waste, require a service life in the range of several decades, since a replacement of a seal is not easily possible. For this reason, we started an accelerated ageing programme for O-ring seals made of HNBR, EPDM and FKM with ageing times up to five years. This paper includes results for samples aged up to one year. A recurring issue for lifetime predictions is the choice of a relevant end-of-lifetime criterion. The standard ISO 11346 mentions 50 % change of the examined property, e.g. elongation at break, as a criterion. For O-ring seals, compression set has often been used as the property defining the end of the lifetime, e.g. with values of 57 % [5] (corresponding to 10 % possible recovery in the reference) or 85 % [6]. However, for O-ring seals, leakage rate is the only characteristic directly correlated to the service life of the sealing system. All other material properties and even compression set can only be indicators, but no criteria for the end of the lifetime by seal failure. For this reason, we are ageing whole components, i.e. O-rings, both uncompressed and compressed between flanges which allows leakage rate measurements on the aged seals. Furthermore, the end of the lifetime determined from leakage rate measurements shall be correlated to more easily measurable properties such as compression set, hardness or viscoelastic loss factor obtained by Dynamic-Mechanical Analysis (DMA). However, care has to be taken to avoid diffusion-limited oxidation (DLO) effects which result in heterogeneous ageing, thus distorting ageing data and lifetime predictions [7-11]. DLO effects can occur depending on oxygen partial pressure, sample dimensions, time, temperature, and material (oxygen permeability). Besides O-rings, sheets of 2 mm thickness were aged to determine material properties for which the O-ring geometry is not suitable or when O-rings would give distorted results because of DLO effects.

Experimental
Materials
The examined O-rings made of commercial elastomers have a cord diameter of 10 mm and an inner diameter of 190 mm. Investigated materials include fluorocarbon rubber (FKM) and ethylene-propylene-diene rubber (EPDM). Both classes of elastomers are applied in containers for radioactive waste. FKM is typically used for high-temperature exposure applications due to its excellent heat resistance and oxidative stability, whereas EPDM is used when low temperature leak tightness is required because of its low glass transition temperature. Additionally, hydrogenated nitrile rubber (HNBR) is tested for comparison as it is another high-performance sealing material used e.g. in automotive or offshore applications. All materials have an initial Shore A hardness of 80. EPDM and HNBR are peroxide-cured and have an upper service temperature (UST) of 150 °C according to the manufacturer, while FKM is bisphenol-cured and has an UST of 200 °C. The used EPDM contains a base polymer with 48 wt% ethylene and 4.1 wt% ethylidene norbornene (ENB) and 50 wt% ethylidene norbornene (ENB) and 50 wt% ethylidene norbornene (ENB) and 50 wt% ethylidene norbornene (ENB) and 50 wt% ethylidene norbornene (ENB) and 50 wt% ethylidene norbornene (ENB).

Figures and tables:
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was compounded with 90 phr of carbon black filler and no plasticizer. The HNBR base polymer has an acrylonitrile content of 36 wt% and an iodine number of 11 (corresponding to approx. 4% residual double bonds) and was mixed with 80 phr of filler (mostly carbon black) as well as 5 phr of plasticizer. FKM contains a polymer with 66 wt% fluorine content and 70 phr of silica and silica-chalk filler.

**Ageing Setup**

O-rings made of these three materials are oven-aged on punched sheets on a rack (Fig. 1a) at four different temperatures (75°C, 100°C, 125°C, and 150°C). They are examined after 1 day, 3 days, 10 days, 31 days, 101 days, 183 days and 366 days. In order to be able to measure properties related to sealing performance such as compression set and leakage rate, samples are also aged compressed between plates (Fig. 1b) with a deformation of about 25% corresponding to the actual compression in service. This approach takes into account the specific geometry and stress state of compressed O-rings. Additionally, samples are aged between flanges (Fig. 1c) that allow leakage rate measurements. Furthermore, sheets of 2 mm thickness are aged suspended from racks. They can be used for determining material properties (e.g. dynamic-mechanical behaviour) for which the O-ring geometry is not suitable or when O-rings would give distorted data because of DLO effects.

**Analysis Methods**

**Material Properties**

Hardness was measured based on DIN EN ISO 868 using Shore A and D hardness. For the measurements, three disks with a diameter of 10 mm, die-cut from 2 mm thick sheets, were stacked to give a sample of 6 mm thickness. Ten stacks were measured and the average is given. For characterizing heterogeneous ageing, IRHD micro hardness measurements were performed (based on DIN ISO 48) on five positions on the O-ring cross-section using a linear table. The measuring points on the cross-section are illustrated in Fig. 2. Slices from the O-ring with a thickness of 3 to 4 mm were used. The given values are average values of five samples.

Dynamic Mechanical Analysis (DMA) subjects the sample to a sinusoidal load over a range of temperature and frequencies. The tangents of the phase lag (tan δ) between stress and strain, called loss factor, is a measure for the viscoelastic behaviour of the material which changes during ageing [12]. From the quotient of stress and strain amplitude, the complex modulus E* can be obtained. From E” and δ, the storage modulus E’ and the loss modulus E” can be calculated which give information about the amount of energy that is stored or lost in a deformation cycle. Additionally, the glass transition temperature range can be determined from the course of these quantities over temperature. Both E” and tan δ exhibit a peak over temperature that can be interpreted as the glass transition temperature (Tg), though T from the peak of tan δ is always higher than that determined from the peak of E”. In this paper the peak of tan δ is used for describing the glass transition temperature.

The measurements were performed in compression mode on a GABO Eplexor 500 device. Data is given for a measurement frequency of 1 Hz. Cylindrical samples with a diameter of 2.5 mm were die-cut from aged sheets of 2 mm thickness and tested in the axial direction of the cylinder.

**Component Properties**

Compression Stress Relaxation (CSR) is a method reflecting the loss of sealing force of a compressed seal over time. Measurements were carried out at 150°C on three O-ring segments per material with a length of approx. 40 mm using EB 02 rigs in an EB 22 oven, both produced by Elastocon, Sweden. Isothermal force measurements were performed every 10 s for the first hour, every minute for the next 23 hours, and afterwards every 10 min. Before the start of the measurements, the samples were conditioned thermally (3 h at 70°C) and mechanically (5 subsequent compressions by 25% followed by instant release) with a day’s rest after each conditioning according to standard DIN ISO 3384. After conditioning, the rigs with the samples were placed in the preheated oven, tempered for 30 min and then compressed by 25%. The force 30 min after the start of compression is the reference force for normalization as described in the standard, as the real force at time zero cannot be determined with this equipment with a minimum measurement rate of one data point every 10 s.

Compression Set (CS) gives information about the resilience of a compressed seal. It is calculated from the initial seal...
height $h_0$, the height $h_1$ of the compressed seal, and the measured recovered seal height $h_2$ by using Eq. 1:

$$CS[\%] = \frac{h_0 - h_2}{h_0 - h_1} \cdot 100\%$$  \hspace{1cm} (Eq. 1)

A CS of 0% would mean a full recovery back to the initial height, while a CS of 100% would mean no recovery from compression at all. CS values above 100% can be obtained if the samples are shrinking during aging. Ten height values were measured on each two O-ring halves with a calliper. However, the recovered height $h_2$ is strongly time-dependent. After 30±3 min, when CS should be measured according to standards ASTM D395 and DIN ISO 815-1, the recovery is still quite fast. As the disassembling of the plates (containing 13 screws) as well as the measurements each took several minutes, the values after 30 min contain an error on the timescale. For this reason, the height was measured three to five days after release when the time-dependency had decreased and the values are closer to equilibrium. Between three and five days, the recovered height changed by a maximum of 0.02 mm or 0.9% CS, which has to be added to the measurement error range of 2-5% CS (including standard deviation of $h_2$ from ten measurements on an aged O-ring and of $h_0$ from ten measurements on five unaged O-rings).

Leakage rate $Q$ is a quantity describing the change in pressure $\Delta p$ of a specific volume $V$ in a specific time period $\Delta t$ and is thus calculated according to Eq. 2.

$$Q = \frac{\Delta p \cdot V}{\Delta t}$$  \hspace{1cm} (Eq. 2)

Leakage rate was measured on O-rings aged compressed between flanges. Three O-rings were aged for each material at each temperature and the average leakage rate is given. After a specific ageing time, the O-rings were tested according to the procedure described below, and then replaced in the ovens for further ageing without changing the compression.

Leakage rate measurements were performed using the pressure-rise method with a set-up shown schematically in Fig. 3. First, $V_2$ is closed and the remaining volume was evacuated to $10^{-2}$ mbar for 8 hours by the pump $P$ for degassing the O-rings. Afterwards, $V_1$ was closed and $V_2$ opened to release the test volume $R_2$ into the total volume ($R_1$, $R_2$ and pipes/hoses). From the resulting pressure (measured by sensor $S_1$ with a working range from $10^{-2}$ to $100$ mbar) the relevant volume $V$ for leakage rate calculation was determined with the ideal gas law. Next, $V_1$ was opened and the total volume $V$ evacuated down to $10^{-2}$ mbar. Then $V_1$ was closed and the pressure rise in the total volume was measured over two hours with sensor $S_2$, which has a working range from $10^{-3}$ to 10 mbar. The leakage rate was calculated from the pressure difference measured in these two hours. The measurements were performed at 20°C. Afterwards, the flange was heated to 60°C (being evacuated simultaneously), and the measurement was repeated. Subsequently, the flange was evacuated and cooled to 25°C (FKM), 30°C (HNBR) or 40°C (EPDM) and again the pressure rise during two hours was measured.

Results & Discussions

Measurements on sheet material

Hardness

Results of hardness measurements on the stacks of sheet material are shown in Fig. 4. For HNBR and EPDM, it was necessary to switch to the Shore D method after some ageing time because of the strong hardness increase. The correlation between the Shore A and Shore D scale was determined by measuring unaged samples on both scales. There 80 Shore A corresponded to 33 Shore D.

The increase in hardness during ageing as observed for HNBR and EPDM can be attributed to crosslinking reactions [13], higher polarity due to oxygen incorporation [14], and, in the case of HNBR, plasticizer loss [15]. For HNBR, crosslinking reactions are dominant [16, 17] and can occur via the alkyl, alkoxy or peroxy radical [18]. On the other hand, both crosslinking (via the termonomer) and chain scission (in the propylene segments) occur in EPDM [17, 19]. As there are many more propylene units than ENB units, scission reactions will dominate, even though the propylene units are more resistant to oxidation than the ENB units. The hardness increase of EPDM is probably due to higher polarity because of incorporation of oxygen, e.g. by the formation of ketone groups as a result of $\beta$-scission in the propylene units.

FKM shows hardly any hardness change during ageing.
Dynamic-Mechanical Analysis

Fig. 5 shows the loss factor $\tan \delta$ vs. temperature for unaged and aged materials. For EPDM and HNBR, the $\tan \delta$ peak is shifted to higher temperatures, meaning that the glass transition temperature ($T_g$) increases with ageing. Besides, the peak value of $\tan \delta$ decreases with ageing for both HNBR and EPDM, indicating a loss of molecular mobility e.g. by an increase in crosslink density [12, 20-22]. After 98 days of ageing at 150 °C, $T_g$ has increased considerably by 38 K for HNBR and by 15 K for EPDM, which also has to be taken into account for applications near the low-temperature limit of the seals [1-3], as $T_g$ has a major impact on the lower service temperature of the material. On the other hand, no change is visible after 98 days at 150 °C for FKM.

Measurements on O-rings

Hardness profiling

As the O-rings are much thicker (Ø 10 mm) compared to the sheets (2 mm thickness), ageing can be influenced by diffusion-limited oxidation (DLO) effects [7, 9, 10, 23]. These effects occur when the oxygen in the interior is consumed faster than it can diffuse in from the surrounding air, leading to a less-aged interior and thus to heterogeneous ageing which distorts ageing data and can lead to overestimated lifetime predictions [11, 24].

Micro hardness measurements across the sample profile (cf. Fig. 2) can give more information about the development of DLO effects [23] and are shown for uncompressed HNBR (Fig. 6) and EPDM (Fig. 7) O-rings. The measurements were not performed in a preferred direction as the O-rings had the same ageing conditions in all directions. As modulus and hardness are related in a non-linear way [13, 25], modulus profiles would show much larger differences between interior and exterior for heterogeneously aged samples.

For HNBR aged at 125 °C and 150 °C, the hardness has increased less in the center of the sample than near the surface. This is probably due to DLO effects which lead to heterogeneous ageing because of less oxygen availability in the interior. The effect is small after 10 days but becomes more pronounced with longer ageing time. On the other hand, EPDM aged for 30 days does not exhibit any hardness inhomogeneities over the cross-section. However, after 101 days of ageing at 150 °C, heterogeneous ageing caused by DLO effects is observed as well.

Compression Stress Relaxation (CSR)

Results of Compression Stress Relaxation tests, performed first at 150 °C to see the largest effects, are shown in Fig. 8. The relaxation is expressed as the ratio of measured force $F$ and initial force $F_0$, which is defined as the force after 30 min of relaxation at the test temperature. Three samples were tested per material, displaying good reproducibility. The test was finished after 55 days because EPDM had reached the end criterion of 10% remaining force.

The observed relaxation is due to both physical effects (e.g. entanglement slippage, relaxation of dangling chain ends [26]) and chemical reactions (e.g. oxidative chain scissions) [19]. FKM demonstrates its advantage as a high-temperature resistant material, exhibiting only little relaxation to 75% over a period of 55 days. In contrast to that, EPDM relaxes to only 10% remaining force in the same time period. HNBR starts with a faster decrease than EPDM, but after about 20 days the decrease levels off. This can be explained by DLO effects that lead to a less aged inte-
ior of the sample (see Fig. 6) which can retain more force.

**Compression Set (CS)**

In general, CS increases with ageing as can be seen in Fig. 9 as crosslinking forms new chemical bonds that are in equilibrium with the compressed geometry, and chain scissions lead to broken bonds that lose their recovery potential [27]. Note that in contrast to hardness and $T_g$, CS of EPDM increases significantly also for ageing temperatures below 150 °C. An explanation is that hardness and $T_g$ are influenced in opposite directions by chain scission and crosslinking reactions during ageing, only leading to slight changes in the measured values, while both reactions types additively increase CS [27]. In Fig. 9, measured CS values are shown as well as photos of the permanently deformed O-rings after 101 days of ageing. The photos correspond to the values in the blue boxes in the diagrams. A CS increase above 100% can be reached if the sample is shrinking during ageing, e.g. due to crosslinking.

A possible procedure to extrapolate the measured data to other temperatures, e.g. room temperature, is the combination of time-temperature shift (TTS) and Arrhenius graph [28]. For TTS, data obtained at different temperatures is shifted along the logarithmic time axis until they superpose [29] which gives a master curve for the temperature that has not been shifted, usually the lowest temperature. The master curves of CS data shifted to 75 °C are shown in Fig. 10. The data can be well superposed except for DLO-affected HNBR samples at 125 °C and 150 °C that give lower CS because of heterogeneous ageing.

In order to extrapolate to other temperatures, the logarithm of the shift factors can be plotted vs. the inverse temperature in an Arrhenius diagram. Ideally, the resulting graph is a straight line that gives the shift factor for shifting the data to the desired temperature. This shifting and extrapolation of measured values to 23 °C is described in detail in [11].

**Leakage rate measurements**

Leakage rate measurements were performed on O-rings aged in flanges. A significant increase in leakage rate was considered to indicate the end of the seal lifetime. Fig. 11 shows that the leakage rate of aged O-rings improved (decreased) slightly compared to the unaged O-rings. One reason for this can be the better adaption of the rubber to the roughness of the seal face with the influence of time and temperature. Additionally, the rather strong decrease of leakage rate of HNBR with ageing can be explained by the increase of crosslink density occurring during ageing of the material [16, 17, 30], leading to reduced permeation of gas molecules through the material [11].

After 98 days of ageing at 150 °C, the O-rings remained leak tight, even though hardness and DMA already indicated strong deterioration of mechanical properties and compression set (CS) values had reached 80 % (HNBR) and 94 % (EPDM). (However, it has to be noted that the shown hardness and DMA data was measured on sheet material. For HNBR aged at 150 °C, O-rings exhibit significantly less ageing effects of bulk properties compared to sheets due to pronounced DLO effects in the O-rings.) However, after 184 days of ageing, CS values exceeded 100% for both HNBR and EPDM, indicating that the recovered height of the O-rings was less than the 7.5 mm spacing between the flanges. Correspondingly, after 184 days at 150 °C EPDM O-rings were completely untight,
meaning that evacuation before leakage rate measurements was not possible as air flowed freely between O-ring and flange. For HNBR, the O-rings were still leak tight at 20 °C and 60 °C. This is probably because the O-rings still stuck to the flanges. This sticking effect was obvious previously during disassembling of the plates to release the O-ring halves aged in compression. Still, one of the three HNBR O-rings aged for 184 days at 150 °C became untight during cooling to -30 °C and remained untight even when tested again at 20 °C. The thermal shrinkage had probably opened up a leak path between the stuck surfaces. As can be seen in Fig. 11, the measured leakage rate of HNBR displays a large scatter, which can explain why only one O-ring became untight. Still, it can be assumed that the O-rings aged for 184 days at 150 °C are not fit for service any more.

The results indicate that O-rings can remain leak tight even when other properties already show strong ageing influence. Similarly, Gillen et al. demonstrated that O-rings can remain leak tight even with only 1 N/cm residual sealing force [14]. This indicates that leakage rate under static conditions is rather insensitive to changes in the material properties, as it displays no negative effects even when material properties have already undergone considerable degradation. For correlating seal failure by increased leakage to material properties, the time of failure needs to be determined more precisely.

Conclusion
Testing of aged HNBR, EPDM and FKM O-rings and sheets revealed significant changes of properties during ageing. HNBR exhibited a strong increase in hardness and T_g as well as a decrease of the viscoelastic loss factor tan δ, probably caused by an increase in crosslink density due to dominant crosslinking reactions during ageing. Besides, HNBR O-rings exhibited diffusion-limited oxidation effects at ageing temperatures of 125 °C and 150 °C which lead to distorted results for compression stress relaxation. EPDM showed similar but less pronounced results like HNBR for hardness and DMA measurements at 150 °C ageing temperature. While hardness of EPDM changed only slightly for ageing temperatures of 75 °C, 100 °C and 125 °C, compression set (CS) increased strongly at all ageing temperatures, probably because chain scission and crosslinking reactions add up to increase CS, while hardness is influenced in opposite directions by these ageing reactions. FKM exhibits superior ageing resistance compared to the other materials, with no change in hardness, a much higher force retention in relaxation experiments at 150 °C and better ageing resistance regarding compression set. Leakage rate measurements showed that O-rings
remained leak tight even when other properties had already deteriorated substantially. This highlights that the choice of the end-of-lifetime criterion has a large influence on the predicted lifetime and that standard criteria referring to material properties do not necessarily correlate with component functions such as static leakage rate.

References