Aging of Elastomeric Seals for Storage Casks – 15080

Anja Kömmling*, Matthias Jaunich*, Dietmar Wolff*
* BAM Federal Institute for Materials Research and Testing, Berlin, Germany
anja.koemmling@bam.de

ABSTRACT

Elastomeric seals are used in many containers, including casks for radioactive waste. However, like all polymers, elastomers are prone to aging, which leads to a loss of sealing force and the ability for recovery which can ultimately result in leakage. Therefore it is important to be able to define an end-of-lifetime criterion and to judge the lifetime of elastomeric seals. For this reason, we started an aging program on three kinds of rubbers (HNBR, EPDM, FKM), monitoring the change of properties at four different aging temperatures over extended periods up to five years. The measured data is used for lifetime prediction by applying a suitable model.

INTRODUCTION

At BAM Federal Institute for Materials Research and Testing in Germany, it is our responsibility to evaluate the safety of casks designed for transport and/or storage of radioactive material. This includes the investigation of elastomeric seals used in the containers. Besides examining the low-temperature behavior of elastomeric seals [1-3], it is our goal to evaluate the service lifetime of the seals with regard to the requirements for long-term safety. With aging, the elastomers can gradually lose their elasticity and their ability for recovery, which might result in a leakage above the allowed level. It is important to know the rate of degradation and to determine which property can be used as a practical and easily measurable end-of-lifetime criterion. For this reason, we started an aging program with selected rubbers for monitoring the change of properties over long periods. Used methods include compression set and compression stress relaxation as measures reflecting the actual behavior of a compressed seal. Additionally, we are applying classical polymer analysis methods like Dynamic Mechanic Analysis (DMA) and Thermo Gravimetric Analysis (TGA) which show changes in the polymeric structure due to chain scission and crosslinking. Hardness is also measured as it is an easy and quick indicator of structural changes in the elastomer. Furthermore, we are testing the leakage rate of the O-rings in order to correlate the changes in physical properties to the actual leak tightness of the seal. This paper presents results for samples aged up to 100 days that were analyzed by DMA, compression stress relaxation and compression set.

EXPERIMENTAL

Materials and Aging Setup

Examined elastomers include fluorocarbon rubber (FKM) and ethylene-propylene-diene rubber (EPDM). These classes of elastomers are used in containers for radioactive waste, either as auxiliary seal in casks containing high level radioactive waste or as main seal in casks for waste with medium or low activity.

FKM is typically used for high-temperature exposure applications due to its excellent heat and oxidative stability; whereas EPDM is used when low temperature leak tightness is required because of its low glass transition temperature range. Additionally, hydrogenated nitrile rubber (HNBR) is tested for comparative reasons as it is another common seal material.
In our aging program, these three materials are oven-aged at four different temperatures (75 °C, 100 °C, 125 °C, and 150 °C) in order to extrapolate the data to service temperature using a suitable model. They are examined after 1 d, 3 d, 10 d, 30 d, 100 d, 0.5 a, 1 a, 1.5 a, 2 a, 2.5 a, 3 a, 3.67 a, 4.33 a, and 5 a. In order to be able to compare between compressed and relaxed rubber, the samples are aged in their undeformed O-ring state (Fig. 1) as well as compressed between plates (Fig. 2) with a deformation of about 25 % corresponding to the actual compression during service. Furthermore, samples are aged in flanges (Fig. 3) that allow leakage rate measurements.

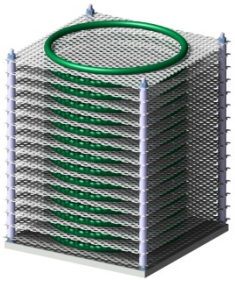


Fig. 1. Undeformed O-rings

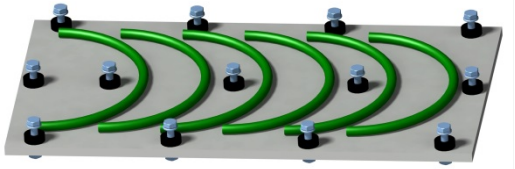


Fig. 2. Half O-rings compressed between plates

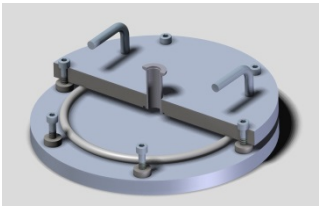


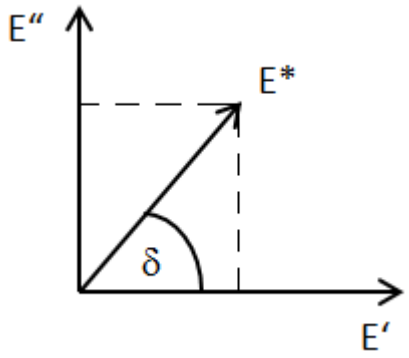
Fig. 3. O-ring in flange for leakage rate measurements

The O-Rings have a cord diameter of 10 mm and an inner diameter of 190 mm.

Dynamic Mechanical Thermal Analysis

The Dynamic Mechanical Thermal Analysis, for short DMTA or DMA, is a very useful tool for characterizing polymers. When putting a sinusoidal load on a polymer, it responds with a deformation that is out of phase to the load due to the viscoelastic nature of the polymer. A DMA device measures this phase difference δ between stress and strain. Tan δ is known as the loss factor as it corresponds to the part of energy that is “lost”, i.e. dissipated in the polymer. Because of changes in the polymer network during aging, tan δ changes as well and is thus a suitable measure of degradation [4]. Additionally, the peak in a plot of tan δ vs. temperature is an indicator for the glass transition process, i.e. the temperature range in which the polymer changes from the hard, glassy state to the rubbery-elastic state. The glass transition temperature can change as well during aging. If chain scission is dominating, the polymer chains have higher mobility and can dissipate more energy, which leads to an increase in tan δ and a decrease of glass transition temperature. On the other hand, if crosslinking is the major degradation mechanism, the elastomer becomes harder and loses its elasticity, which means that it can dissipate less energy and tan δ decreases [4]. This would also result in an increase in glass transition temperature, which can be critical for low-temperature applications as the glass transition temperature relates to the lowest service temperature of a seal.
From the quotient of stress amplitude and strain amplitude, the complex modulus E* can be obtained. The complex modulus can be divided into storage modulus and loss modulus. The

storage modulus E’ correlates to the elastic energy stored in the material and shows a strong decrease over the glass transition range. The loss modulus E” correlates to the amount of energy dissipated in the material and shows a maximum over temperature that can be interpreted as the glass transition temperature. The parameters tan δ, E*, E’ and E” are related as illustrated by Fig. 4 and the following equations.



$$E' = |E^*| \cdot \cos\delta \qquad \text{(Eq. 1)}$$

$$E'' = |E^*| \cdot \sin\delta \qquad \text{(Eq. 2)}$$

$$\tan\delta = \frac{E''}{E'} \qquad \text{(Eq. 3)}$$

Fig. 4. Relation of complex modulus E*, storage modulus E', loss modulus E", and phase shift δ in the complex plane.

The change of the peak value of tan δ and the shift in glass transition temperature are the most relevant parameters for our aging investigation.
All the values given in the results section were obtained with a measuring frequency of 1 Hz on a GABO Eplexor 500 device.
The samples were prepared from slices of 2-3 mm thickness cut from the aged O-ring. From these slices, samples of 2.5 mm diameter were die-cut near the surface and from the center of the slice, as shown in Fig. 5. This enables detecting heterogeneous aging, as caused e.g. by diffusion-limited oxidation (DLO) [5-7] effects.

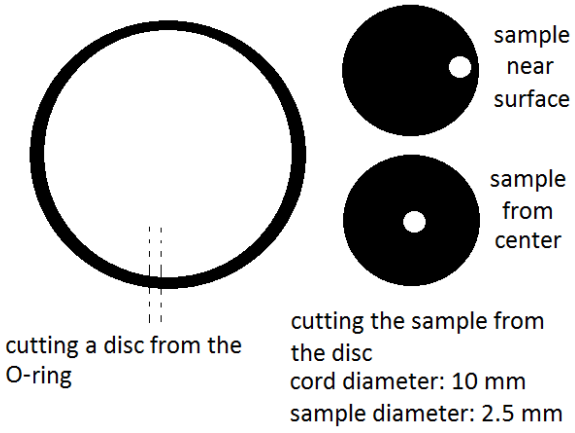


Fig. 5. DMA sample preparation.

Compression Stress Relaxation

Compression stress relaxation is a useful measurement directly relating to the seal in its application. In order to maintain its function, the seal has to exert a certain force on the sealing areas. The lower this sealing force F is in comparison to the initial value F_0, the more likely the seal is to leak, especially during dynamic loads. Therefore compression stress relaxation experiments, i.e. monitoring of the recovery force of a 10 mm segment of the seal, have been carried out in an Elastocon device on the basis of standard DIN ISO 3384. The same temperatures and compression as in the oven-aging experiments have been used.

Compression Set

A useful method yielding information about the recovery behavior of seals is compression set (CS). In the respective standard DIN ISO 815-1, the compression set is calculated from the measured height h_2 30 min after release, the initial height h_0 and the compressed height h_1 with the following formula:

$$CS\ [\%] = \frac{h_0 - h_2}{h_0 - h_1} \cdot 100\ \% \qquad \text{(Eq. 4)}$$

A compression set of 0 % means a full elastic recovery back to the initial height h_0, while a compression set of 100 % means no recovery at all when the seal remains at its compressed height h_1. Deviating from the standard, the compression set was measured on whole O-rings instead of standard test pieces as these values are more relevant for our investigations. Furthermore, CS was measured several days instead of 30 min after release from compression in order to be closer to the equilibrium value.

RESULTS & DISCUSSION

Dynamic Mechanical Thermal Analysis (DMA)

In Fig. 6 a-c below, the graphs for storage modulus E', loss modulus E" and loss factor tan δ are shown for each unaged material at a measuring frequency of 1 Hz.

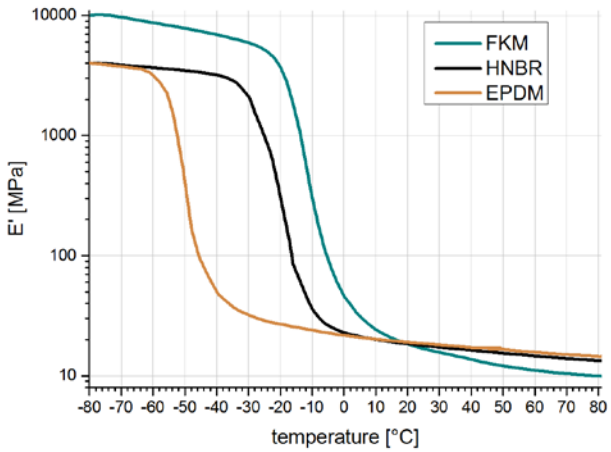


Fig. 6a

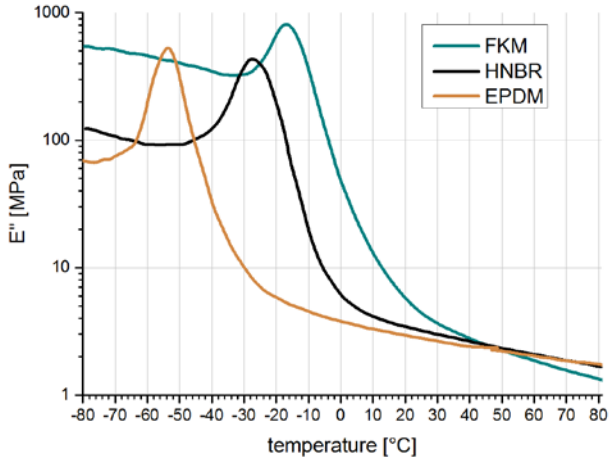


Fig. 6b

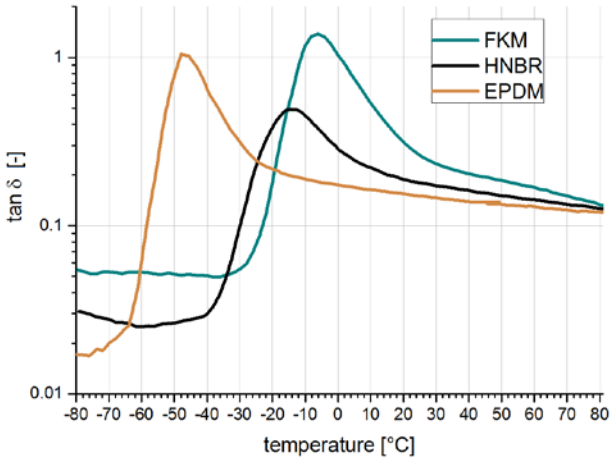


Fig. 6c

Fig. 6. DMA graphs measured at 1 Hz for each unaged type of elastomer
a) storage modulus E', b) loss modulus E", c) loss factor tan δ

Each parameter shows a characteristic course around the glass transition temperature (T_g). The storage modulus changes over two decades, while the other two graphs show a peak. From each graph a T_g can be determined, e.g. from the inflection point of E', which is usually similar to the peak in E". However, the T_g value is influenced by many factors, such as heating rate, measurement frequency and evaluation method, see [8].
The graphs show the characteristics of the different materials. At 23 °C, all materials have a similar storage modulus. This corresponds well with the fact that all materials have the same hardness, as hardness and modulus are related properties. Furthermore, the different glass transition ranges are apparent, with EPDM exhibiting a much lower glass transition temperature than the other two materials.

Fig. 7 shows the change in glass transition temperature obtained from the peak in the E" graph for uncompressed HNBR, both near the surface and in the center of a sample (cf. Fig. 5).

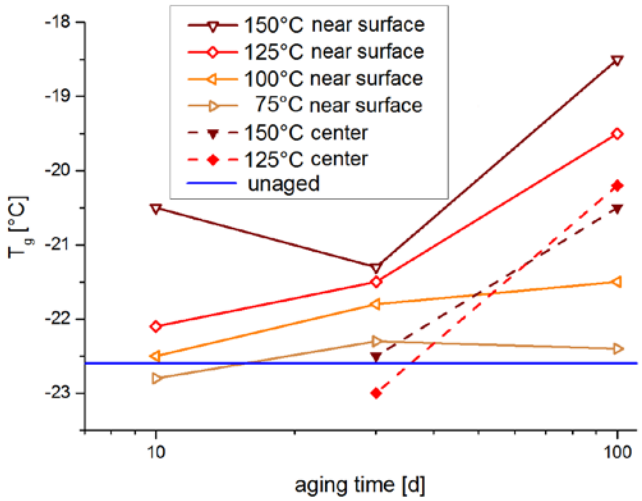


Fig. 7. Change of glass transition temperatures (T_g) over aging time for uncompressed HNBR at a measuring frequency of 1 Hz. The value of the unaged sample is indicated by the blue line.

The figure reveals that the aging process leads to complex changes in the material. However, a general trend for an increase in T_g with aging time is observed, which indicates that crosslinking reactions dominate. At 125 °C and 150 °C, the glass transition temperature determined from the center of the sample has lower values than near the surface. This is an indicator for diffusion-limited oxidation (DLO) effects. Further investigations over the sample profile, e.g. by micro hardness measurements, could give more information about the extent of DLO effects [7] and are in progress.

Changes during aging can be observed in all of the DMA measures mentioned in the Experimental section. However, the modulus values are dependent on sample geometry. This could lead to uncertainties as the shape of the die-cut sample changes slightly when the sample becomes harder during aging. For this reason, tan δ is used as the representative measure. Fig. 8 shows the change of the peak value of tan δ during aging of uncompressed HNBR.

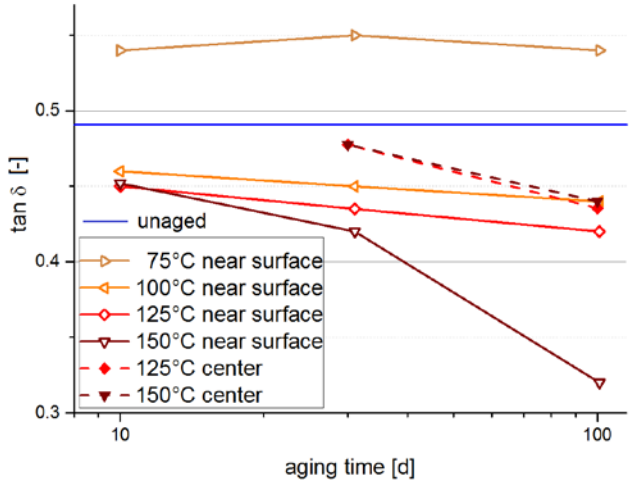


Fig. 8. Change of tan δ over aging time for uncompressed HNBR at a measuring frequency of 1 Hz. The value of the unaged sample is indicated by the blue line.

Except at 75 °C, tan δ decreases during aging which can be interpreted as a loss in E" or an increase in E' (see Eq. 3). This can also be explained by crosslinking reactions [4], confirming that crosslinking is the major degradation mechanism in HNBR. The differences between samples near the surface and from the center at 125 °C and 150 °C are apparent as well.
Data for the other materials is in progress.

Compression Stress Relaxation

Compression stress relaxation data for FKM and EPDM at 150 °C are shown in Fig. 9. Three samples were tested for each material, though the scattering appears to be low.

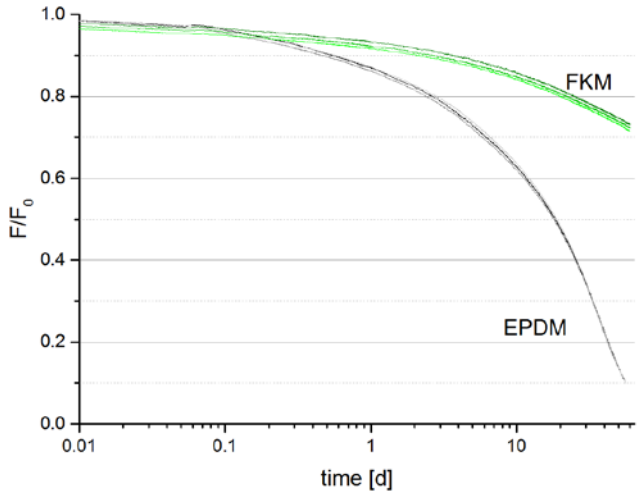


Fig. 9. Sealing force decay of FKM and EPDM at 150 °C.

Both materials show a continuous decrease of the F/F_0 ratio over time. Without any chemical aging effects, the force would be expected to converge toward an equilibrium value. However, when chemical reactions occur, new bonds are formed that are in equilibrium with the compressed geometry and have no driving force for recovery [9]. Additionally, chains are broken that lose their recovery potential as well. This means that the force exerted by the rubber can converge to zero.
Once again, FKM shows its superiority as a high-temperature material, exhibiting only little relaxation to 75 % over a period of 55 days, while EPDM relaxes to only 10 % remaining force in the same time period. The test for HNBR is still running and has reached about 40 % remaining force after 40 d. Such a strong force decrease in EPDM over this relatively short period questions the long-term applicability of this material at 150 °C as specified by the manufacturer.
Experiments at the lower temperatures will follow.

Compression Set

Fig. 10 - 12 show the remaining compression of O-rings with initially circular cross-section after 100 d of aging in compression at different temperatures.

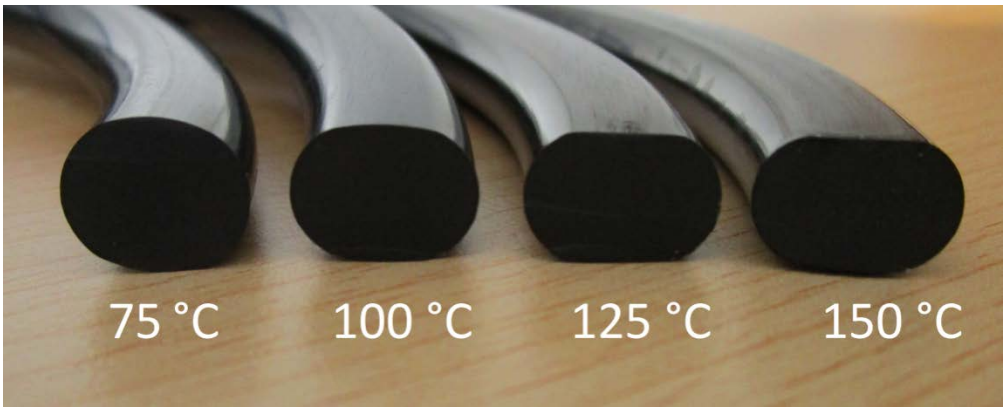


Fig. 10. Compression set of HNBR after 100 d of aging at the indicated temperatures.

Fig. 11. Compression set of EPDM after 100 d of aging at the indicated temperatures.

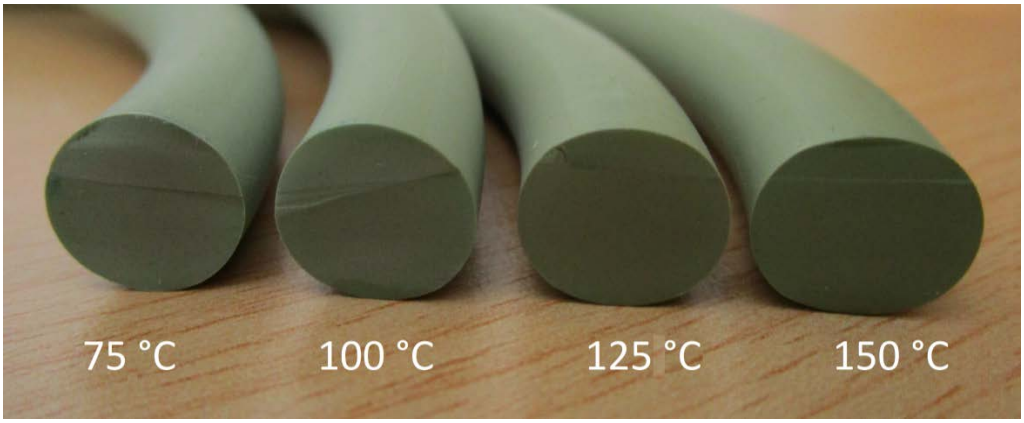


Fig. 12. Compression set of FKM after 100 d of aging at the indicated temperatures.

It can be seen that HNBR shows a permanent compression at all temperatures, while EPDM and FKM still show almost circular cross-sections at 75 °C and 100 °C. Due to strong sticking to the

plates after aging at 125 °C and 150 °C, a thin surface layer was torn off the EPDM O-rings during dismounting which resulted in the visible rough surfaces.

Fig. 13 (a-c) show the CS of the compressed samples after aging.

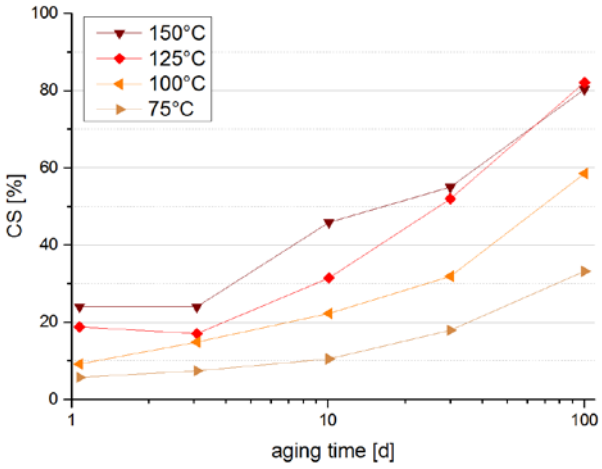


Fig. 13a

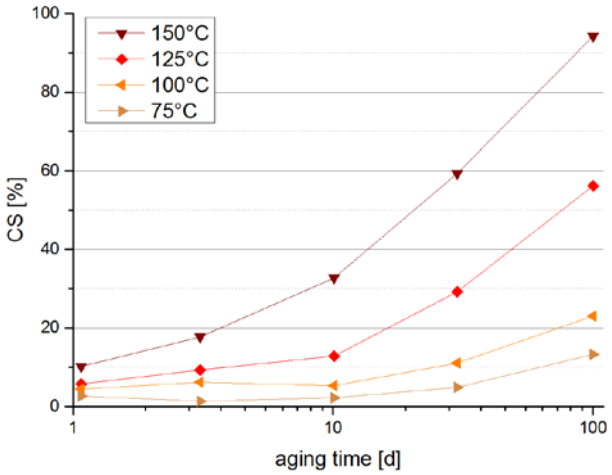


Fig. 13b

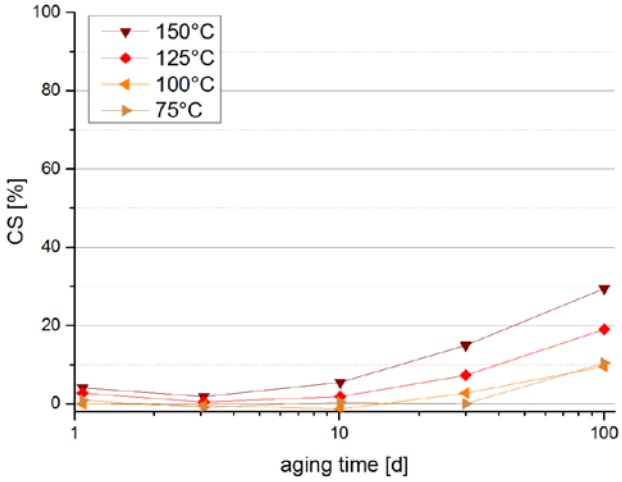


Fig. 13c

Fig. 13 (a-c). Compression set (CS) of samples aged with 25 % compression; (a) HNBR, (b) EPDM, (c) FKM.

At the highest aging temperature of 150 °C, the compressed EPDM has already reached a compression set of 95 %, while HNBR and FKM have reached 80 % and 30 %, respectively. With such high compression sets of 80 % and 95 %, the EPDM and HNBR seals exhibited only little elastic recovery after release. The values for HNBR at 150 °C are close to the ones at 125 °C after 30 d or more of aging which could be explained by DLO effects. When the outer part of the sample consumes most of the oxygen or forms an oxygen diffusion barrier, the inner part of the sample at 150 ° is protected from oxidation and can retain its elastic properties [7].

Lifetime Prediction

There are several generally accepted possibilities of using the data for lifetime predictions. When data are available at different aging times and at different aging temperatures, the time-temperature-superposition applicable to viscoelastic polymers can be used by shifting the curves of higher temperatures along the logarithmic time axis until they superpose with a curve at a lower temperature [10]. This is shown in Fig. 14 for the CS of EPDM.

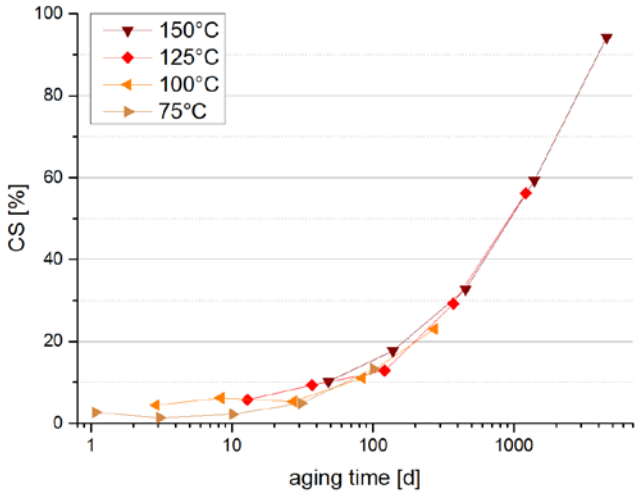


Fig. 14. Time-temperature data from Fig. 8b shifted to 75 °C for compression set (CS) of EPDM

This gives a master curve for the temperature that has not been shifted, usually the lowest temperature (75 °C in this case). According to the shift, the highest measured compression set of 95 % would occur after around 4500 days ~ 12 years at 75 °C. However, this plot is only reliable if the reaction mechanisms at the higher aging temperatures are the same as at lower temperatures. The Arrhenius plot (natural logarithm of the shift factors a_T vs. the inverse temperature [11]) in Fig. 15 indicates that this might not be the case, as the slope and thus the activation energy of the aging mechanism appears to change over the temperature range.

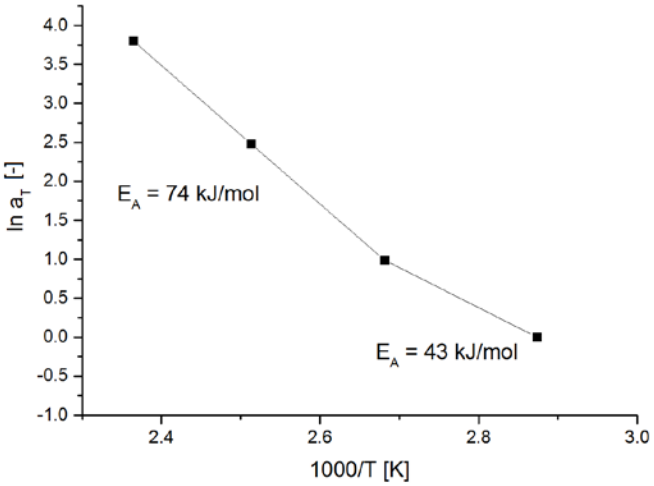


Fig. 15. Arrhenius plot of logarithm of shift factors (a_T) vs. inverse temperature.

In theory, the Arrhenius plot should show a straight line that would allow extrapolation to lower temperatures. However, it can be seen that the slope changes towards lower temperatures. This behavior has been reported before for EPDM [12] and probably originates in the large examined temperature range in which the Arrhenius assumption of unchanging chemical mechanisms does not apply. For instance, it is well known that higher temperatures enable chemical reactions that would not be activated at lower temperature. Thus, aging experiments at temperatures much higher than the service temperature are of limited value for lifetime predictions and can dangerously lead to over-confident predictions.

CONCLUSION AND OUTLOOK

We have started an aging program on three types of elastomers and obtained results for aging up to 100 d. Changes observed with the DMA method were an increase in glass transition temperature and a decrease of tan δ values in HNBR which both indicate crosslinking as the major degradation mechanism. In a compression stress relaxation (CSR) experiment, EPDM has degraded to 10 % remaining force after 55 d at 150 °C. The compression set (CS) of samples aged in compression increases with aging temperature and time. After 100 d at 150 °C, EPDM and HNBR have reached compression sets of 80 % or higher. FKM shows only minor signs of degradation in CS and CSR yet. The CS data of EPDM allows a time-temperature superposition that can be used for lifetime prediction. However, these extrapolations should be treated with caution. With further data we hope to be able to understand the aging process better and to give more realistic and practical lifetime predictions for elastomeric O-rings.

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