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Long-term Behavior of Elastomer Seals and Polymers for Neutron Shielding

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Abstract

The long time-frame of the necessary safe enclosure of radioactive waste in containers gains internationally an increasing attention. Extended storage periods as well as an usually necessary subsequent transportation after storage have to be evaluated.

In Germany, the concept of dry interim storage in dual purpose metal casks before disposal is being pursued for spent nuclear fuel (SNF) and high level waste (HLW) management. The initially planned and established dry interim storage license duration of up to 40 years will be too short and its extension will become necessary since there is no repository available in due time.

The main safety relevant components are the thick-walled dual purpose metal casks. These casks consist e.g. of a monolithic cask body with integrated neutron shielding components (polymers, e.g. polyethylene) and a monitored double lid barrier system equipped with metal and elastomer seals. The metal seals of this bolted closure system guarantee the required leak-tightness, whereas the elastomer seals allow leakage rate measurement of the metal seals.

At BAM we focus on the long-term performance of the sealing system and neutron shielding materials as their application conditions are considered as rather demanding.

Therefore, BAM began to investigate the overall function and long-term behavior of elastomer and metal seals and also the irradiation influence on neutron shielding materials.

Recently a new project was initiated to expand our investigations to obtain more and in some context better applicable data.

This paper describes the approach of our new research project with the aim of further closure of existing knowledge gaps and presents an overview of investigations concerning the low temperature behavior of elastomer seals, of running long-term tests on elastomer seals at different temperatures under static conditions and the influence of gamma irradiation on neutron shielding materials.

Introduction

In general, the packaging of radioactive material is designed for comparatively long time scales. Due to the already existing delays in the siting procedure of a deep geological repository for spent nuclear fuel and high level waste, as well as in construction of the already licensed Konrad repository for low and intermediate level waste, even longer periods of interim storage become more relevant in Germany. BAM is involved in most of the cask licensing procedures and especially responsible for the evaluation of cask-related long-term safety issues and therefore interested in the performance of safety relevant components. As described in one of our recent papers the long-term performance requirements resulting from application conditions in radioactive waste packages are manifold compared with other application areas as e.g. automotive, aviation or process engineering [1]. Depending on the terms of use of the specific container, these requirements include:

- long-term use up to several decades
- radiation effects resulting from the inventory
- operation at elevated temperatures and at possible low temperatures during transport or within the storage facility
- mainly under purely static conditions but potentially highly dynamic events in case of accidents

Therefore, BAM began to investigate the overall function and long-term behavior of elastomer and metal seals and also the irradiation influence on neutron shielding materials.

Recently a new project was initiated to expand our investigations to get more and in some contexts better applicable data.

This paper describes the approach of our new research project on the long-term behavior of metal and elastomer seals as well as polyethylene as safety relevant components of transport and storage casks for radioactive material (LaMEP) with the aim of further closure of existing knowledge gaps and it presents an overview of running long-term tests on elastomer seals at different temperatures under static conditions and the influence of gamma irradiation on neutron shielding materials. Additionally, some results concerning low temperature behavior of elastomer seals are discussed. The results of the investigations of metall seals are part of the paper presented by Wolff et al. [2].

The paper is sectioned into two parts. In the first part, an overview of elastomer seal investigations is given and in the second part selected results on the effect of gamma irradiation on neutron shielding materials are presented.

Investigations concerning elastomer seals

Elastomer seals are an essential component of nearly all technical systems by ensuring the safe and reliable operation of e.g. combustion engines, chemical reactors or containers.

Elastomer seals are applied in transport and storage containers as static seal between the container body and the bolted lid. Therefore the performance under possible temperatures and over long time scales is of interest.

Low temperature behavior and sealing performance

The low temperature behavior of elastomer seals is of high interest for many applications and was therefore studied by several researchers [3-7]. It is mainly important in the context of container transport as the transport regulations require full performance of the cask even at -40 °C. Therefore, the seal is also required to be fully functional at this temperature. With this motivation BAM launched an investigation program which focused on the dependence of seal performance on temperature and on the correlation with material changes occurring at low temperatures. The results were published in e.g. [8-12]. The correlation between the occurring changes of material properties due to the glass-rubber transition and the seal performance under purely static conditions indicate that the seal remains leak tight even at temperatures below the glass-rubber transition (typical values e.g. from Differential Scanning Calorimetry (DSC) measurements). This could be explained by the relation of the compression force (generating the observed dependence of the failure temperature on degree of compression), the frequency dependence of the glass-rubber transition, and the mismatch of thermal expansion coefficients.

Effects of dynamic events, which could occur e.g. in accident conditions, were tested with a new experimental setup for partial seal decompression. The setup allows compression of an O-ring with an inner diameter of 190 mm and a cord thickness of 10 mm by 25 % and a partial seal decompression of this compression within one second by 0.2 mm corresponding to a remaining compression of 23 % (degree of compression is therefore reduced by 8 % of the initially applied compression). In parallel to the partial seal decompression, the leakage rate is measured by a pressure rise method. Results for an fluorocarbon rubber (FKM) material are discussed in [13]. In Figure 1 some results are shown.

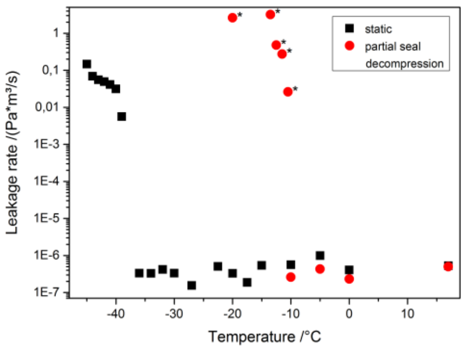

Figure 1 Leakage rate of a FKM seal determined without and with partial release of the seal at different temperatures [13].

When the release was performed at room temperature, no effect is observed as the leakage rate before the release remains unchanged during release. However, when the experiment was performed at lower temperatures, it was detected that the temperature at which a leakage could be observed was about 20 °C higher as for purely static tests. This shows that even if the seal can remain leak tight in case of slow enough changing temperatures, the temperature influence can become prominent in the frequency dependence of the elastomer behavior. In contrast to static conditions, the ability of fast recovery which is necessary to remain leak tight in the release experiment is lost already at much higher temperatures as indicated by e.g. thermal analytical methods [13].

Aging investigations on elastomer seals

It is our goal to understand the aging process to be able to evaluate the service lifetime of seals with regard to the requirements for long-term safety. With aging elastomers can gradually lose their elasticity and their ability for recovery [14, 15], which might result in a leakage rate above the allowed level. To get a better understanding of the aging processes an aging program with selected rubbers (HNBR (hydrogenated nitrile butadiene rubber), EPDM(ethylene propylene diene rubber), FKM) was started for monitoring the change of properties at different temperatures (75 °C, 100 °C, 125 °C, 150 °C) over long periods of time. The focus is on the long time scale of the planned experiments which is a clear difference to other typical aging programs. But as doubts about the applicability of the often assumed Arrhenius extrapolation model exist [16, 17], we try to get a broader data base by using several temperatures and long aging periods. The test program includes the aging of whole components, i.e. O-rings, both uncompressed and compressed which is another distinction to standardized approaches which use standard test samples instead of components. With our approach it is possible to measure leakage rates on the aged seals and thus to determine the most important property of the sealing system. A further aim is to determine a suitable end-of-lifetime criterion.

However, care has to be taken to avoid diffusion-limited oxidation (DLO) effects which can occur when oxygen consumption in the sample is faster than oxygen diffusion from the surrounding air into the sample, thus resulting in a less-aged interior of the sample. This leads to heterogeneous aging which can result in distorted aging data and overestimated lifetime predictions [16, 18, 19].

In Figure 2 the Shore D hardness of uncompressed O-rings is shown in dependence on aging time at different temperatures.

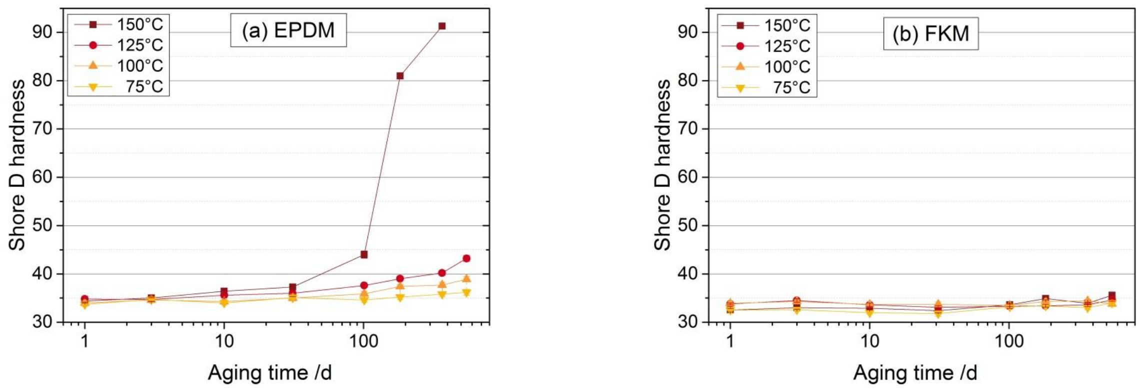

Figure 2 Shore D hardness of EPDM and FKM in dependence of aging time at different temperatures

The increase in hardness during aging as observed for EPDM can be attributed to crosslinking reactions [20] and possibly higher polarity due to oxygen incorporation [21]. FKM shows hardly any hardness change during aging up to now. The results from compression set (CS) are shown in Figure 3. The values were determined three to five days after release from samples aged in compression of 25 % at different temperatures.

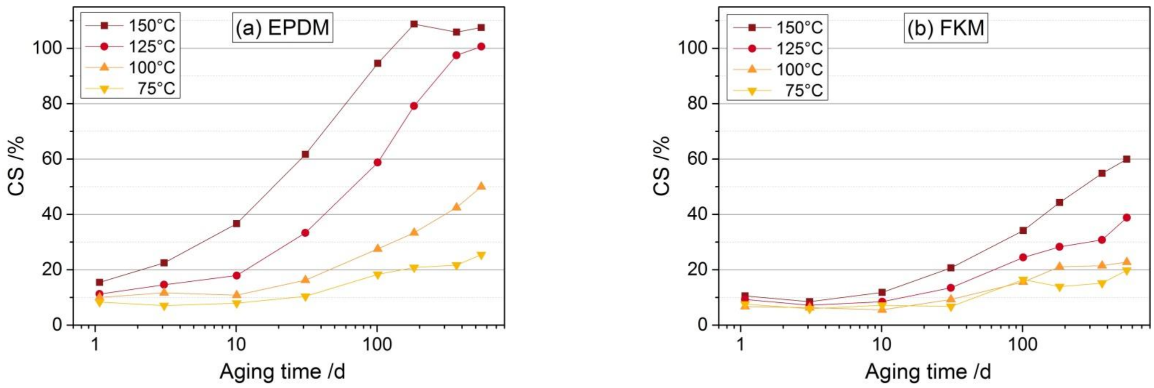

Figure 3 Compression Set (CS) of EPDM and FKM in dependence of aging time at different temperatures

The CS increases with aging as crosslinking forms new chemical bonds that are in equilibrium with the compressed geometry, and chain scissions lead to broken bonds decreasing the recovery potential of the elastomer [22]. Note that in contrast to hardness, the CS of EPDM and FKM increases significantly also for aging temperatures below 150 °C. An explanation is that hardness is influenced in opposite directions by chain scission and crosslinking reactions during aging, only leading to slight changes in the measured values, while both reactions types additively increase CS [22]. A CS increase above 100 % can be reached if the sample is shrinking during aging, e.g. due to crosslinking. While the possible recovery of the seal decreases and in parallel also the sealing force drops, the sealing performance, given as leakage rate, remains sufficient. In Figure 4 the leakage rate of the compressed O-rings are shown for several aging times at 125 °C.

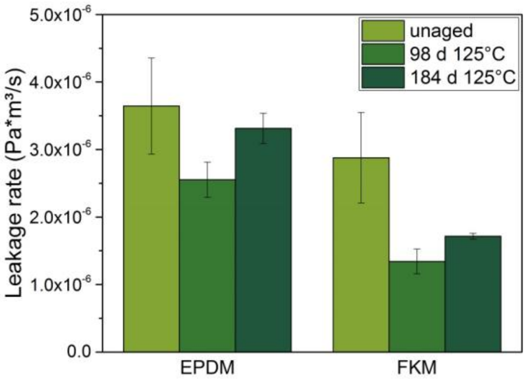

Figure 4 Leakage rate of EPDM and FKM after aging for different times at 125 °C

Thus the O-rings remained leak tight even when other properties had already deteriorated quite strongly. A comparable result was reported by Gillen et al. [21] when aged O-rings remained leak tight even with a remaining line load of only 1 N/cm. However, all three measured flanges with EPDM seals aged at 150 °C were untight after about half a year of aging.

In the case of HNBR aging at higher temperatures pronounced heterogeneous aging caused by diffusion-limited oxidation effects is detected.

Effect of gamma irradiation on neutron shielding materials

With regard to the long-term application of ultra-high and high molecular weight polyethylenes (U)HMW-PE as neutron shielding material, it is necessary to understand the influence of gamma irradiation on the material properties. For this purpose we investigated samples which were gamma irradiated at Synergy Health Radeberg GmbH with doses from 50 kGy up to 600 kGy. Afterwards a comparison was made with untreated material [23].

During the use of the neutron shielding material within the wall of the container, the material is not only exposed to irradiation but is thermally treated in parallel. This combination of thermal aging and radiation is inherent to the application and the resulting material changes should not have a safety relevant influence on container performance. Therefore, the effects of high temperature exposure in combination with subsequent or previous irradiation are investigated with a comprehensive aging program including thermal aging at 125 °C for aging periods of 30 days, 0,5 years, 1 year, 3 years and 5 years and irradiation with doses of 50, 100, 200, 400 and 600 kGy.

Parts of the results presented here have been taken from previous publications [24, 25]. A more detailed discussion can be found in the corresponding papers.

The observed material changes indicate a crosslinking of the material caused by irradiation. This is shown e.g. in Figure 5 displaying the insoluble content of the samples which increases with irradiation dose. The insoluble content of about 30 % of the untreated material can be related to physical crosslinks (e.g. entanglements) as a result of the very long polymer chains of the UHMW-PE.

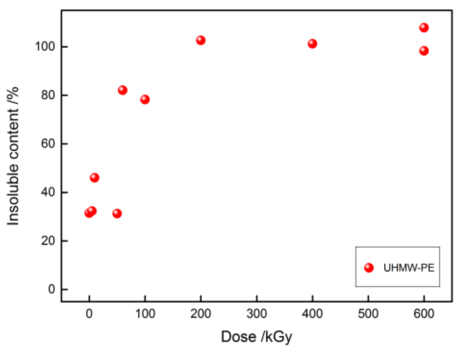

Figure 5 Insoluble content of UHMW-PE in dependence of irradiation dose

A further indication for an increase of the degree of crosslinking is an increase of the plateau value of shear modulus G' [23]. Additional effects are an increase of the degree of crystallinity and a discoloration of the materials which increases with dose [23]. An example for the discoloration of irradiated samples is shown in Figure 6.

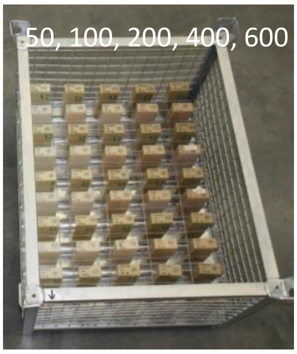

Figure 6 Irradiated (U)HMW-PE-samples before thermal aging

Preliminary results indicate that the discoloration is partly reversible under the influence of elevated temperatures, especially in the case of UHMW-PE. Additionally the thermal treatment leads to an decrease in crystallinity. Further investigations are performed for elucidating the structural changes leading to the discoloration and its reversal.

With regard to the special application of (U)HMW-PE as neutron shielding material in casks for storage and transport of radioactive material, the detected changes of the irradiated (U)HMW-PE are not safety relevant for long-term utilization over a period of 40 years in Germany [24, 26].

Investigations in the near future include component test to study the influence of sample dimensions on thermal expansion and creep behavior of the polyethylene materials. In parallel the effect of irradiation on samples that were first thermally aged will be studied.

Conclusions

The investigations performed at BAM on the long-term performance of sealing systems and neutron shielding materials as components of containers for radioactive waste contribute to closing existing knowledge gaps. This knowledge is required for possible storage period extensions as well as for a necessary subsequent transportation after storage.

The running project on long-term behavior of metal and elastomer seals as well as polyethylene as safety relevant components of transport and storage casks for radioactive material (LaMEP) comprises three topics namely the long-term behavior of metal seals, elastomer seals and polyethylene. The here discussed aging of elastomer seals reveals that different materials show quite distinct aging behavior. The static seal function is maintained even with very severe changes of the material properties.

Polyethylene used as neutron shielding material shows several changes caused by irradiation which are related to the formation of additional crosslinks and chain scissions. In addition, hydrogen is released from the material during irradiation. The increased crosslink density has an influence on the performance of the material but so far no safety relevant issues could be identified for the application in containers.

Acknowledgments

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