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INVESTIGATION OF ELASTOMER SEAL BEHAVIOR FOR TRANSPORT AND STORAGE PACKAGES

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ABSTRACT

Rubbers are widely used as main sealing materials for containers for low and intermediate level radioactive waste and as additional component to metal seals in spent fuel and high active waste containers. According to appropriate guidelines and regulations safe enclosure of the radioactive container contents has to be guaranteed for long storage periods as well as down to temperatures of -40 °C for transportation. Therefore the understanding of seal behavior is of high importance.
In this paper we focus on the behavior of elastomer seals at low temperatures with regard to potential decrease of leak-tightness. In addition, changes in material properties due to aging effects over long periods of time and their influence on the seal performance is investigated.
It is known that material properties of rubbers are strongly temperature dependent. At low temperatures this is caused by the rubber-glass transition (abbr. glass transition). During continuous cooling, the material changes from rubber-like entropy-elastic to stiff energy-elastic behavior, that allows nearly no strain or retraction due to the glass transition. Hence rubbers are normally used above their glass transition but the minimum working temperature limit is not defined precisely.
Aging of elastomer seals is important, as possible dynamic loads may have to be considered during the whole interim storage period (so far approved in Germany for up to 40 years) and for transportation after storage.
For the investigations, fluorocarbon (FKM) and ethylene-propylene-diene (EPDM) rubbers were selected as they are often used in radioactive waste containers. Some materials were purchased from a commercial seal producer and some materials were compounded and cured at BAM. The elastomers where studied by several thermo-analytical methods and compression set to characterize the material behavior at low temperatures. Additionally component tests were performed to determine the breakdown temperature of the sealing function of complete elastomer O-rings.

INTRODUCTION

Rubbers are widely used as main sealing materials in containers for low and intermediate level radioactive waste and as additional component to metal seals in spent fuel and high active waste containers. They are applied due to their special material properties and easy use [1]. This application

leads to many challenging requirements for the essential reliable operation of the seal. 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 as well at elevated temperatures and at possible low temperatures during transport or within the storage facility
- mainly under pure static conditions but potentially highly dynamic events in case of accidents

There are several other applications where some of these requirements also apply as e.g. water pipes of different kinds (static and long-term) or automotive applications (at least some dynamic parts, temperature variations) but the full set of requirements is not often encountered. Additionally, for many applications replacement is much easier and common practice.

Therefore reliable long-term experience is rare. Combined with the challenging tightness requirements it is necessary to understand the seal behavior at different temperatures and over long periods of time.

In the following several aspects of relevant phenomena are stated that should be addressed in more detail considering the special needs resulting from the application:

1. The fundamental sealing process is not well understood concerning the structure-property and the property-function relationship. Which property of a seal influences its performance in which way?
   What are the requirements for extended storage and transport after storage?
2. The question of the temperature dependence of several properties should be addressed and the consequences for the application have to be considered.
3. Which changes occur due to aging over extended periods of time at elevated temperatures and under irradiation. It is known, that typical aging effects of elastomers can be caused by oxidation, irradiation and temperature [2]. The consequence can be additional crosslinking and/or chain scission.

To address these gaps we started to investigate the behavior of elastomer seals at low temperatures with regard to potential leak-tightness changes [3-5]. In the course of this investigation also a new method for characterization of elastomer seal materials has been developed [6, 7] that emulates the compression set measurement but can be performed semiautomatic and much faster than standardized procedures according to [8, 9].

Especially for judgement of the long-term performance accelerated experiments have to be performed. There are several standards that describe how to determine aging effects and how to interpret them (see e.g. [10, 11]). These standards generally use a lifetime criterion and assume an Arrhenius-like behavior of the aging process. The question whether this assumptions are correct, especially for the extrapolation over very long periods of time is under discussion and several studies imply non-Arrhenius behavior, e.g. [12]. This is the reason for us to actually prepare an extensive experimental aging program with several materials.

The aging will be performed in temperature chambers at different temperatures and the samples will be uncompressed and compressed as well. To get information about the sealing performance additional seals mounted in test flanges will be aged parallel to the samples. Our aim is to quantify the

effect of the storage condition, develop an appropriate aging model and to get an insight how this model is affected during the course of the aging process.
For this paper the low temperature properties are in focus. Here several methods are presented and their results are discussed.
It is known that material properties of rubbers are strongly temperature dependent. At low temperatures this is caused by the rubber-glass transition (abbr. glass transition). During continuous cooling, the material changes from rubber-like entropy-elastic to stiff energy-elastic behavior, that allows nearly no strain or retraction due to the glass transition. Hence rubbers are normally used above their glass transition but the minimum operational temperature limit is not defined precisely.
Aging of elastomer seals is important, as possible dynamic loads may have to be considered during the whole interim storage period (so far approved in Germany for up to 40 years) and for transportation after storage.
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METHODS

Differential Scanning Calorimetry (DSC)

DSC evaluates the change in temperature difference between a sample crucible and a reference crucible during continuous temperature change or under isothermal conditions. The temperature difference is used to calculate the heat flow into or out of the sample. Characteristic changes in heat flow indicate melting, evaporation of volatiles, glass transition and also chemical reactions by the release or uptake of heat [13-15]. DSC is the most common method for determination of glass transition temperatures, but these values correlate with the change in heat capacity during glass transition which is not directly correlated with the seal function.
The used device was a DSC 204 F1 from Netzsch. The heating rate was 10 K/min and the measurement was performed under a nitrogen atmosphere with a flow rate of 20 ml/min.

Dynamic Mechanical Analysis (DMA)

The DMA is a scientific mechanical testing technique that can be applied for temperature dependent determination of viscoelastic material properties, namely the storage and the loss component of the material stiffness [16, 17].
The principle of DMA is that an oscillating stress is applied to the sample, and the displacement of the sample is measured. From the stress and the phase shift between force and displacement the viscoelastic material properties (storage and loss modulus) can be determined.
During glass transition the storage and the loss modulus show a distinct behavior, and from the curves glass transition temperatures can be determined. As these values are directly correlated with the change of the material stiffness during glass transition, a correlation with seal behavior is likely.
The measurements were performed with a Netzsch DMA 242 C. At first the samples were measured in a classical DMA experiment with a heating rate of 1 K/min and amplitude of 40 µm. The measurements were performed by using a single cantilever set up that uses a free bending length of 5 mm and a frequency of 1 Hz.

Compression Set (CS)

The compression set measurement determines the amount of deformation that is not recovered after a certain amount of time since sample release. Before the start of the measurement the sample is compressed by a given percentage (typically 25 %) and stored for a defined time at test temperature.

As the standardized compression set procedure according to [8, 9] is rather laborious, time consuming and yields only single point values, an accelerated procedure using DMA was developed [6]. The compression sample holder was used to measure the DMA compression set (CS_{DMA}). The experiments were performed according to the temperature and force program given in Figure 1.

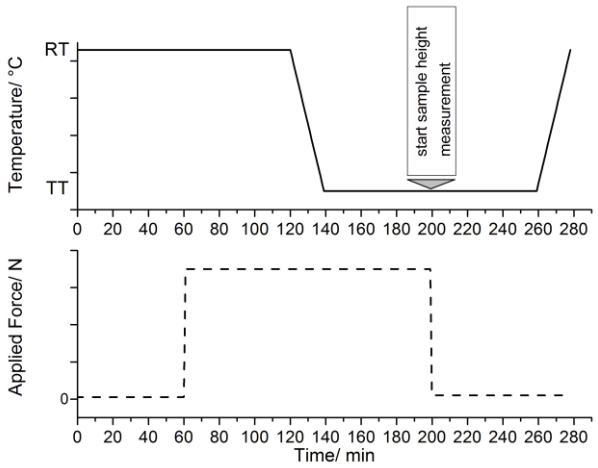

Figure 1. Temperature and force program of the CS_{DMA} at a temperature below room temperature

The temperature and force program has two parts. In the first part the sample is kept at room temperature (RT) for 60 min to equilibrate the temperature, then it is compressed over 60 min at RT by a force close to the maximum of the DMA equipment. Then the temperature is decreased to the respective test temperature (TT) that can be chosen arbitrarily within the temperature range of the measurement equipment. After 1 h of equilibration at the selected temperature the compressed sample height h_c is determined and the second part of the experiment begins. During the second part the height recovery is measured after reducing the compression force to a small residual value. The residual force value is necessary to ensure contact between probe and sample.
The sample height $h_1(t)$ is measured at the test temperature. As sample geometry a cuboid with an edge length of about 2 mm is used. The initial height of the uncompressed sample (h_0) is determined before the measurement.
With the $h_1(t)$ data the CS_{DMA} values can be calculated by using equation 1:

$$CS_{DMA} = \frac{h_0 - h_1(t)}{h_0 - h_c} * 100 \quad \% \qquad (1)$$

The value of sample height is measured approximately every 10 seconds. The measurement can be performed as long as necessary and afterwards the sample is heated again to room temperature. The temperature dependence of the CS_{DMA} is measured by repetition of the measurement program at different temperatures.

Component Tests

To measure the function of the seal a test flange was constructed that enables the measurement of leakage rates by the pressure rise method. In combination with a controlled low temperature cabinet the leakage rate can be measured at different temperatures. Therefore the temperature of the seal is independently measured with thermocouples. The device is schematically shown in Figure 2.

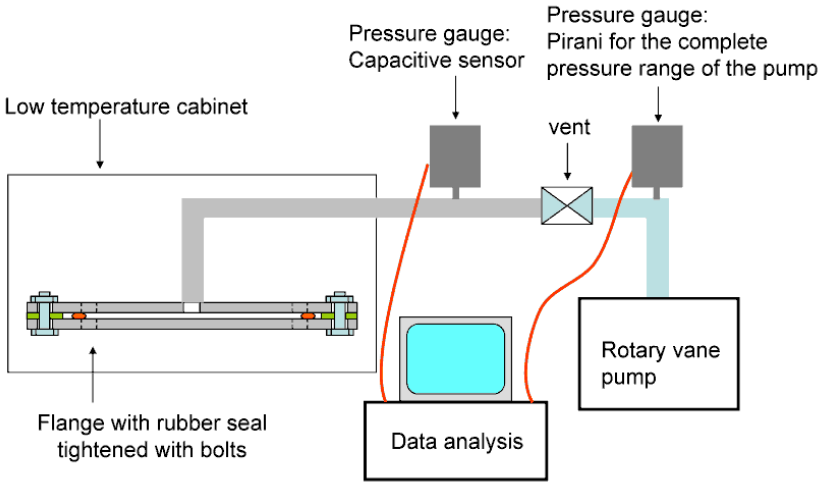

Figure 2. Measurement setup for the determination of the leakage rate over temperature [4]

The measurements where performed in two parts. At first the temperature within the low temperature cabinet was decreased stepwise starting at room temperature until a clear increase in leakage rate was detected. In the second part the temperature was increased to observe whether the leakage rate will reduce again.

RESULTS AND DISCUSSION

Thermal analysis

The performed measurements give an overview of the temperature dependent material properties, especially of the low temperature region showing the glass transition temperature range indicated by a heat flow step in the DSC thermogramm and a step-like decrease in storage modulus. The result of the DSC and DMA measurements are given exemplarily in Figure 3.

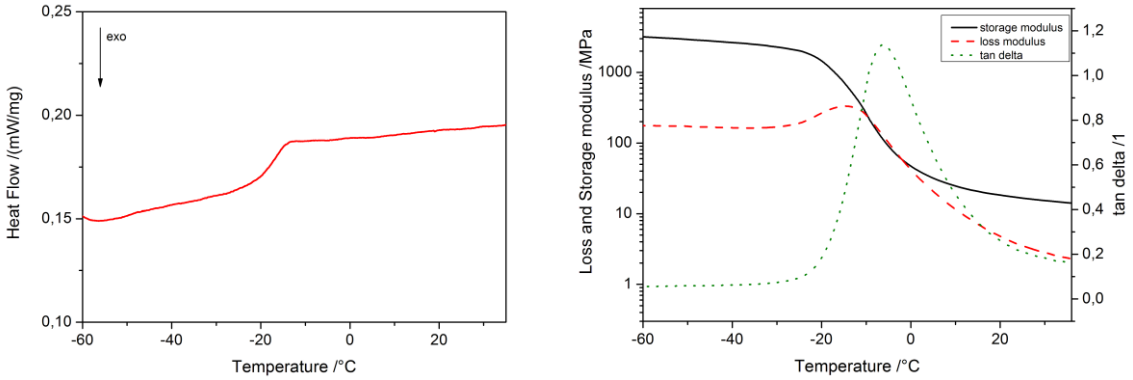

Figure 3. left: DSC-Thermogram of FKM with a heating rate of 10 K/min, right: Storage (E') and loss modulus (E'') measured by DMA with a heating rate of 1 K/min [18]

The storage modulus of the material shows rather constant decrease with increasing temperature up to -25 °C, afterwards a step-like reduction is detected between -25 and -5 °C. At higher temperatures only slight temperature dependence is observed in the rubbery region. As for DSC the step-like decrease of storage modulus can be used for the description of the glass transition.
The values of the glass transition temperatures (T_g) determined from DSC- and DMA-measurements are given in Table 1.

Table 1. Different glass transition temperatures of the FKM sample determined by DMA at 1 Hz with a heating rate of 1 K/min from a linear plot and DSC with a heating rate of 10 K/min [7]

Measurement method and applied definition of the glass transition temperature	*EPDM 1*	*EPDM 2*	*NBR*	*FKM*
DSC-extrapolated onset	-57 °C	-57 °C	-35 °C	-21 °C
DSC-inflection point	-54 °C	-53 °C	-31 °C	-17 °C
DSC-extrapolated offset	-52 °C	-52 °C	-28 °C	-14 °C
E'-extrapolated onset (1 Hz)	-61 °C	-60 °C	-36 °C	-23 °C
E'-inflection point (1 Hz)	-56 °C	-55 °C	-31 °C	-17 °C
E'-extrapolated offset (1 Hz)	-51 °C	-52 °C	-26 °C	-11 °C
tan δ-peak (1 Hz)	-51 °C	-52 °C	-22 °C	-10 °C
E''-peak (1 Hz)	-55 °C	-55 °C	-30 °C	-16 °C

As can be seen from the data, already for the measuring frequency, the glass transition process covers a broad temperature range. The different definitions of the glass transition temperatures vary considerably. Therefore it is highly important to define the measurement and analysis technique used to determine a glass transition temperature. Without this definition a single value is close to meaningless. Additionally it should be kept in mind, that the glass transition process is dynamic and can be influenced by the heating rate and the frequency of the measurement. But if the definition of the procedure of glass transition determination is given the values can be quite useful.

Compression Set

The results of compression set measurements were described in detail in [3, 5-7]. It was shown that the CS_{DMA} values are strongly dependent on temperature and on the time since stress release.
Results of the CS_{DMA} measurements are shown for several materials in an isochronal plot in Figure 4. This kind of plot allows a quick comparison of the material behavior at different temperatures. Therefore the data taken at the same time after stress release from continuous measurements at several temperatures are used.

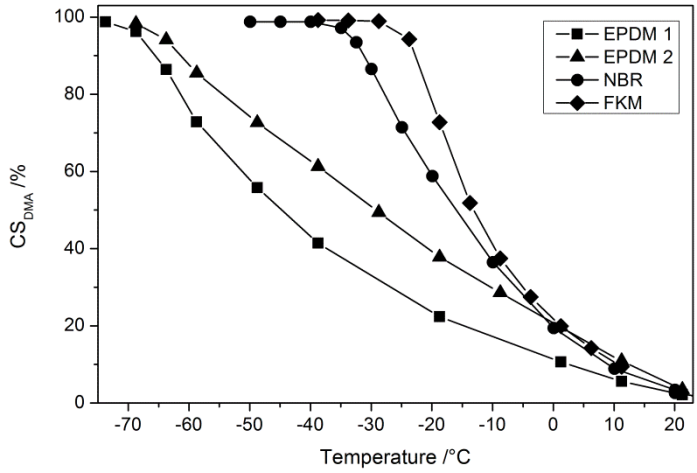

Figure 4. Compression set of different materials at 30 min after stress release shown as function of temperature (from [7])

A strong change of CS_{DMA} can be seen in the region of the glass transition. For every isochronal curve a region is observed where the decrease in CS_{DMA} is strongest. This region shifts to lower temperatures with increase of time.

Component Tests

In Figure 5 an example for the performed leakage rate measurements on a FKM-rubber with 25 % compression is shown.

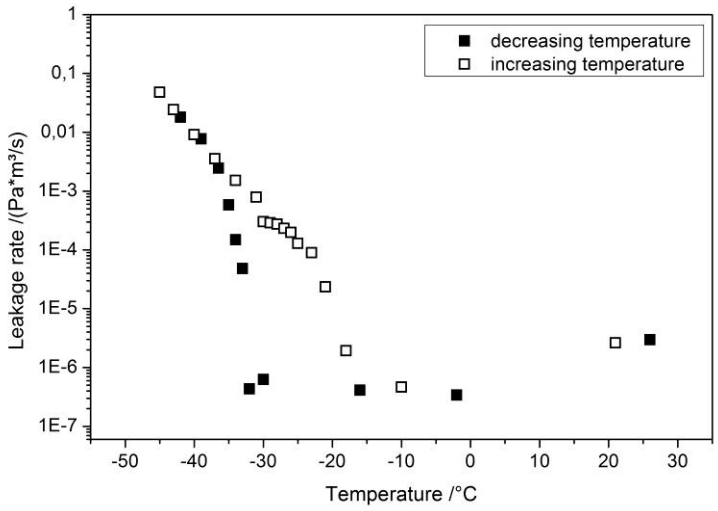

Figure 5. Leakage rates determined at different temperatures for a FKM with a degree of compression of 25 % [19]

Over a broad temperature range the leakage rate is not influenced by a decrease in temperature. But below -34 °C a strong increase in leakage rate is observed. A leakage pathway is formed that increases with further decreasing temperature. By subsequently increasing the temperature, the leakage rate decreases. But the initial value is attained at a much higher temperature in comparison to the beginning of the formation of the leakage path on cooling. The temperature of the leakage path formation lies lower as the corresponding glass transition temperatures determined by DSC and DMA, this can be explained under consideration of the thermal expansion behaviour of the seals and the flange and the forces induced during the mounting process.

CONCLUSION

For many applications it is important to ensure the safe operation of seals. The application conditions of rubber seals in storage and transport containers are challenging and several aspects especially concerning the low temperature and long-term properties are not completely understood today.

The presented results help to characterize the performance of a seal manufactured from these materials. A seal can only work under dynamic conditions if the seal material is able to react fast enough to changes of the outer dimensions of the sealing groove due to external forces. If the reaction of the material is slower than the changes in the dimensions of the sealing groove a leakage path is formed. This path can be closed again by a sufficient amount of recovery of the material.

The measurement of time dependent recovery of a compressed elastomer at low temperatures expressed as compression set with a DMA worked very well. It turned out, that the compression set measurement is able to give valuable information to differentiate the material behavior of various compounds.

In the component test the strong increase in leakage rate under the applied static test conditions occurs at a considerably lower temperature compared with glass transition temperatures from DSC or DMA measurements. This can be explained by consideration of the thermal expansion behavior of seal and surrounding flange. The subject of ongoing research will cover the aging process to ensure the proper function of applied seals not only at different temperatures but also during extended storage periods.

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