



UNDERSTANDING THE LOW TEMPERATURE PROPERTIES OF RUBBER SEALS

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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. The safe encapsulation of the radioactive container inventory has to be guaranteed according to legislation and appropriate guidelines for long term storage periods as well as down to temperatures of -40 °C during transport.

Therefore the understanding of failure mechanisms that lead to leakage at low temperatures is of high importance.

It is known that the 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 behaviour, 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, what can cause problems during application. Therefore the lower operation temperature limit of rubber seals should be determined in dependence of the material properties.

The results of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) are combined with the results of standardized measurements as the compression set according to ISO 815. To reduce the test time of the standard tests a faster technique was developed.

Additionally, the breakdown temperature of the sealing function of complete O-ring seals is measured in a component test setup to compare it with the results of the other tests. The experimental setup is capable of measuring the leakage rate at low temperatures by the pressure rise method.

A fluorocarbon rubber (FKM) was selected for this investigation as it is often used for radioactive waste containers. Some materials (seals and test sheets) were purchased from a commercial seal producer and some materials were compounded and cured at BAM in form of rubber sheets.

INTRODUCTION

Elastomers are often used for different sealing applications due to their special material properties and easy use [1]. In transport and storage containers they are also applied to ensure a safe encapsulation of the radioactive waste.

The safe encapsulation of the radioactive container inventory has to be guaranteed according to legislation and appropriate guidelines for long term storage periods as well as down to temperatures of $-40\text{ }^{\circ}\text{C}$ during transport. Therefore the understanding of the failure mechanisms causing the rise in leakage rate at low temperatures is of high importance.

It is known, that the material properties of an elastomer are limited in temperature by the rubber-glass transition (abbreviated: glass transition) during which the material changes between a rubber like entropy-elastic to a stiff, energy-elastic behaviour [2]. In the glassy state the seal can not recover the elastic deformation and the sealing force drops.

Several testing techniques can be used to measure the material properties at low temperatures. On the one hand thermo analytical methods are used to determine the glass transition temperature and tests like the compression set are used to determine the material behaviour at different temperatures. The aim of our work is to correlate the results of classical thermo analytical methods, measuring different material properties, with the function of the seal to get a better understanding of the lower operation temperature.

The applied methods include Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and the Compression Set (CS) measurement. To measure the compression set a new technique was applied that is described in Jaunich et. al. [3, 4]. This technique, gives results comparable to the compression set test according to ISO 815-2:2008 [5] but uses the advantage of the DMA device i.e. the continuous measurement of sample thickness during recovery and the possibility to define a whole test program for many temperatures that is then automatically measured within a relatively short time.

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 at the outside of the seal is additionally measured with a thermocouple. The device is schematically shown in Figure 1.

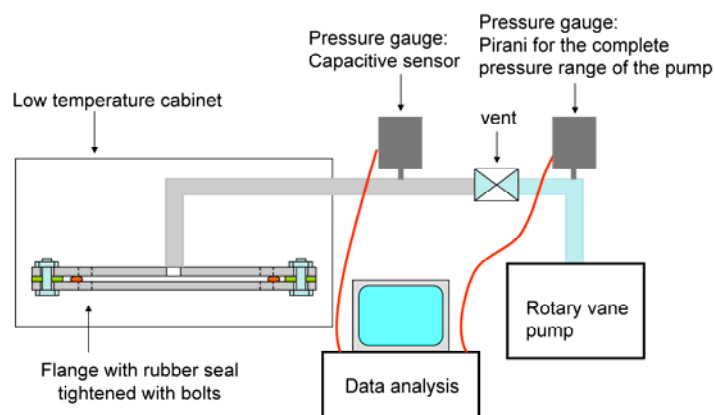


Figure 1: Measurement setup for the determination of the leakage rate over temperature.

First results of measurements performed with this setup are shown in the corresponding PATRAM oral presentation but in this paper the measurement of the physical properties are in focus.

MATERIALS

For the investigation a fluorocarbon rubber (FKM) was selected. In spite of their high price these specialty elastomer class is commonly used for certain applications for transport containers of

dangerous goods [6]. The advantages of FKM are their high temperature stability and their chemical resistance.

The used sample material V3681-80 was purchased from the Parker Hannifin GmbH & Co. Kg. It has a Shore A hardness of 80 and is except for its colour (green) a typical FKM material.

METHODS

Differential Scanning Calorimetry

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.

To analyse the observed typical step-like change in the heat flow curve, that is caused by the change of heat capacity due to glass transition [7], three straight lines are fitted to the data [8].

Dynamic Mechanical Analysis

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 [9, 10].

The principle of DMA is that an oscillating stress is applied to the sample. 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.

The measurements were performed with a Netzsch DMA 242 C. At first the materials were measured in a classical DMA experiment in the temperature range from -90 to 50 °C with a heating rate of 1 K/min and amplitude of 40 µm. The samples are measured in a single cantilever set up that uses a free bending length of 5 mm.

Compression Set

As the standardized compression set procedure is rather pedestrian, time consuming and yields only single point values, an accelerated procedure using DMA was developed [4]. 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 2.

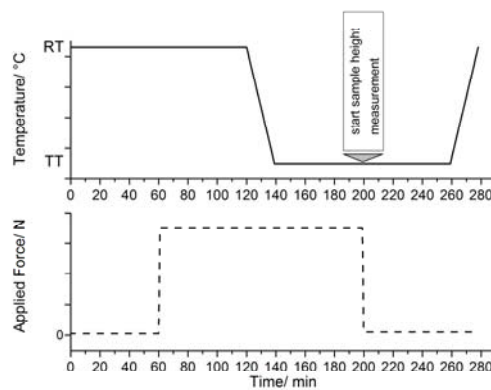


Figure 2: Temperature and force program of the CS_{DMA} at a temperature below room temperature.

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 lowered 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 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:

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

The value of sample height is measured approximately every 10 seconds. After additional 60 min the sample is heated again to room temperature.

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. The result of the DSC measurement is given in Figure 3. The glass transition region lies in the range from -21 to -14 °C.

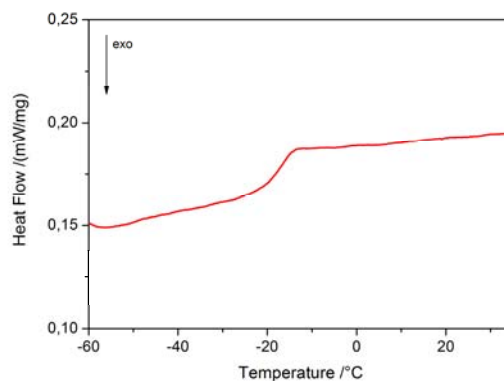


Figure 3: Thermogram of FKM with a heating rate of 10 K/min.

The results of conventional DMA measurements are shown in Figure 4.

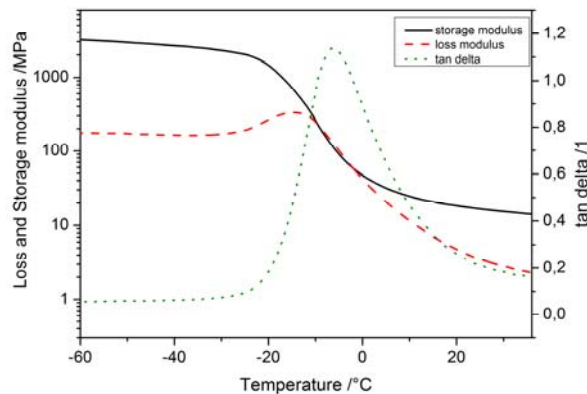


Figure 4: Storage (E') and loss modulus (E'') measured with a heating rate of 1 K/min.

The storage modulus of the material shows rather constant decrease with rising temperature up to $-25\text{ }^{\circ}\text{C}$, afterwards a step-like reduction is detected between -25 and $-5\text{ }^{\circ}\text{C}$. At higher temperatures only slight temperature dependence is observed in the rubbery region. As for DSC the step-like decrease can be used for the description of the glass transition. Therefore three lines are fitted to the step and the intersection is used as onset respectively offset value. 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.

method	T_g
DSC: Heat flow-onset	$-21\text{ }^{\circ}\text{C}$
DSC: Heat flow-inflection point	$-17\text{ }^{\circ}\text{C}$
DSC: Heat flow-offset	$-14\text{ }^{\circ}\text{C}$
DMA: E' -onset	$-25\text{ }^{\circ}\text{C}$
DMA: E' -inflection point	$-19\text{ }^{\circ}\text{C}$
DMA: E' -offset	$-11\text{ }^{\circ}\text{C}$
DMA: $\tan \delta$ -peak	$-6\text{ }^{\circ}\text{C}$
DMA: E'' -peak	$-15\text{ }^{\circ}\text{C}$

As can be seen from the data, already for the measuring frequency, the glass transition process covers a broad temperature range from -25 to $-6\text{ }^{\circ}\text{C}$. 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 values are defined, they can be quite useful.

It is expected that the CS_{DMA} values show even more pronounced temperature dependence.

Compression Set

The results of the CS_{DMA} measurements are shown in Figure 4.

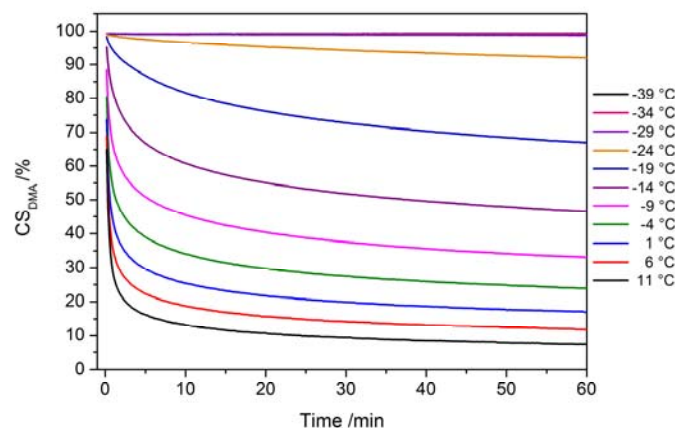


Figure 4: Results of CS_{DMA} measurement at different temperatures between 11 to $-39\text{ }^{\circ}\text{C}$.

At higher temperatures the CS drops fast at the beginning of the measurement and shows than a slow decrease with time. With decreasing temperature the initial step-like decrease becomes smaller but the behaviour at longer times seems to be unchanged. At temperatures below $-29\text{ }^{\circ}\text{C}$ the material shows a constant compression set value of about 100 %. This means that the material is totally stiff and shows no recovery. The named temperatures lie beneath the measured glass transition temperatures and therefore the material is in the glassy state. This indicates that the onset temperature of the glass transition process has a clear impact on the compression set values. In Figure 5 isochronal datasets derived from the CS_{DMA} data shown in Fig. 4 are plotted.

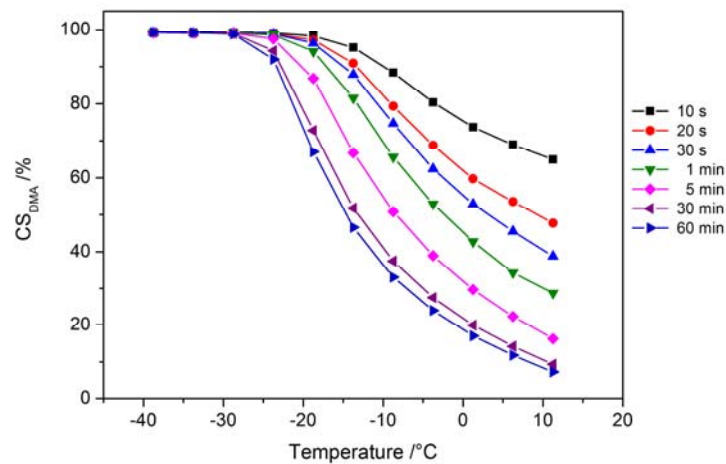


Figure 5: Isochronal plots of the CS_{DMA} values over temperature.

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

CONCLUSION

The investigation of low temperature properties of elastomeric sealing materials by means of thermo analytical methods is a sound way to get information about the glass transition process. But for comparison of measurement results a definition of the glass transition temperature that incorporates the measurement and analysis technique is required.

The measurement of time dependent recovery of a compressed elastomer at low temperatures as performed during the compression set test gives additional information about the function of a seal at low temperatures and the contact between seal and flanges. The applied compression set measurement by DMA gives similar results to the standard technique. But it allows measuring the properties over a wide temperature range within a considerably shorter time. This method is well suited for a fast preselection of different materials.

At temperatures in the region of the glass transition, between -6 and $-25\text{ }^{\circ}\text{C}$, the FKM material shows no spontaneous rebound and the speed of recovery becomes lower with decreasing temperature. At temperatures below $-29\text{ }^{\circ}\text{C}$, where the material is completely within the energy elastic state, the material shows no recovery of the applied compression.

The time-temperature dependency of recovery is very important for the performance of a seal under dynamic conditions. A seal can only preserve leak-tightness if its material is able to react fast enough to changes of the outer dimensions of the sealing groove due to external forces. If the



response of the material is slower than the changes in the dimensions of the sealing groove a leakage path is formed. This leakage path can be closed again by a sufficient amount of recovery of the material if a sufficient operating temperature can be realized.

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