Behaviour of Neutron Moderator Materials at High Temperatures in CASTOR®-Casks: Qualification and Assessment

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1. Introduction

The Federal Institute for Materials Research and Testing (BAM) is the responsible German authority for the assessment of mechanical and thermal designs of transport and storage casks for radioactive materials. BAM checks up the proofs of the applicants in their safety reports and assesses the conformity to the Regulations for the Safe Transport of Radioactive Material [1, 2]. One applicant is the Gesellschaft für Nuklear-Behälter mbH (GNB) with a new generation of transport and storage casks of CASTOR®-design.

GNB typically uses ultra high molecular weight Polyethylene (UHMW-PE) for the moderation of free neutrons. Rods made of UHMW-PE are positioned in axial bore holes in the wall of the cask and plates of UHMW-PE are in free spaces between primary and secondary lid and between the bottom of the cask and an outer plate (Figure 1). Because of the heat generated by the radioactive inventory and because of a strained spring at the bottom of every bore hole, UHMW-PE is subjected to permanent thermal and mechanical loads as well as loads from gamma and neutron radiation. UHMW-PE has been used under routine- and normal conditions of transport for maximum temperatures up to 130 °C. For new generations of CASTOR®-design maximum temperatures will be increased up to 160 °C. That means a permanent use of UHMW-PE at temperatures within and above the melting region of the crystallites.

In this paper, some results of special investigations for the proofs of usability of UHMW-PE at temperatures up to 160 °C under real conditions of transport and storage in CASTOR®-casks are given. For that, investigations on temperature dependent expansion behaviour under laboratory conditions as well as in large scale experiments, especially in the case of multiple heating and cooling, were done. Besides, geometrical creep strength for long-term loading by temperatures and pressures with regard to the chemical and physical stability properties of UHMW-PE above the melting region of crystallites were analyzed. BAM took part in the tests implemented by GNB and assessed the results in the sense mentioned above.

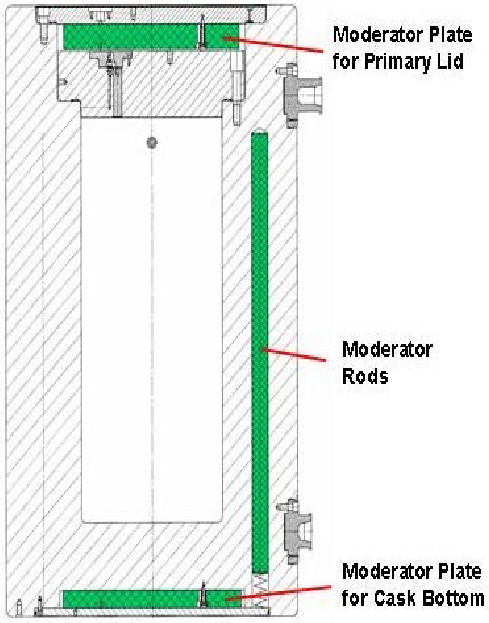

Fig. 1 Design of UHMW-PE in CASTOR®-casks

2. Ultra high molecular weight Polyethylene

Raw materials of UHMW-PE in powder form have a very high averaged molar mass of about $5.0 \cdot 10^6$ g mol^{-1}. That is why, starting from the powder form, pressings are produced by a special sintering process with an external pressure. From the pressings, round rods and plates are produced by metal-cutting manufacturing. The resulting properties of the UHMW-PE are anisotropic. One can differentiate between the pressure direction during the sintering process and all the plate directions perpendicular to that pressure direction. For the positioning of the round rods in the plates it has to be distinguished between lengthwise (perpendicular to the pressure) and cross direction (parts from pressure direction and parts perpendicular to the pressure) of the rods. The anisotropic behaviour of the materials is partly reduced by a special annealing procedure of these pressings during several days. Unfortunately, full reductions of the intrinsic stresses are impossible because of the high molar mass of the macromolecules of UHMW-PE. UHMW-PE has a minimum density of 0.935 g cm^{-3} at a standard ambient temperature. The tensile stresses F150/10 are near 0.22 ± 0.05 MPa. The thermal expansion coefficients depend on temperatures and on direction with maximum values near 600•10^{-6} K^{-1}. When exceeding the melting temperature of crystallites near 135 °C, UHMW-PE undergoes a phase transition from a semi-crystalline to an amorphous state. However, it keeps a rubber-elastic behaviour up to 250°C. That means the location of the macromolecules with respect to each other can change. Anyway, the chemical structure of the macromolecules remains stable with preservation of the basic properties.

3. Thermal expansion behaviour as a function of temperature

Thermal expansion coefficients of original round rods for CASTOR®-casks were measured by GNB in the temperature range from 130°C to 250°C. Figure 2 shows measured values lengthwise and cross direction as well as design values defined on the basis of measured values. Lengthwise and cross direction values show a strong increase in the melting region between 130° and 140 °C where the materials changes from a tight and semi-crystalline structure to a less tight amorphous structure. Local maxima of coefficients of thermal expansion exist at

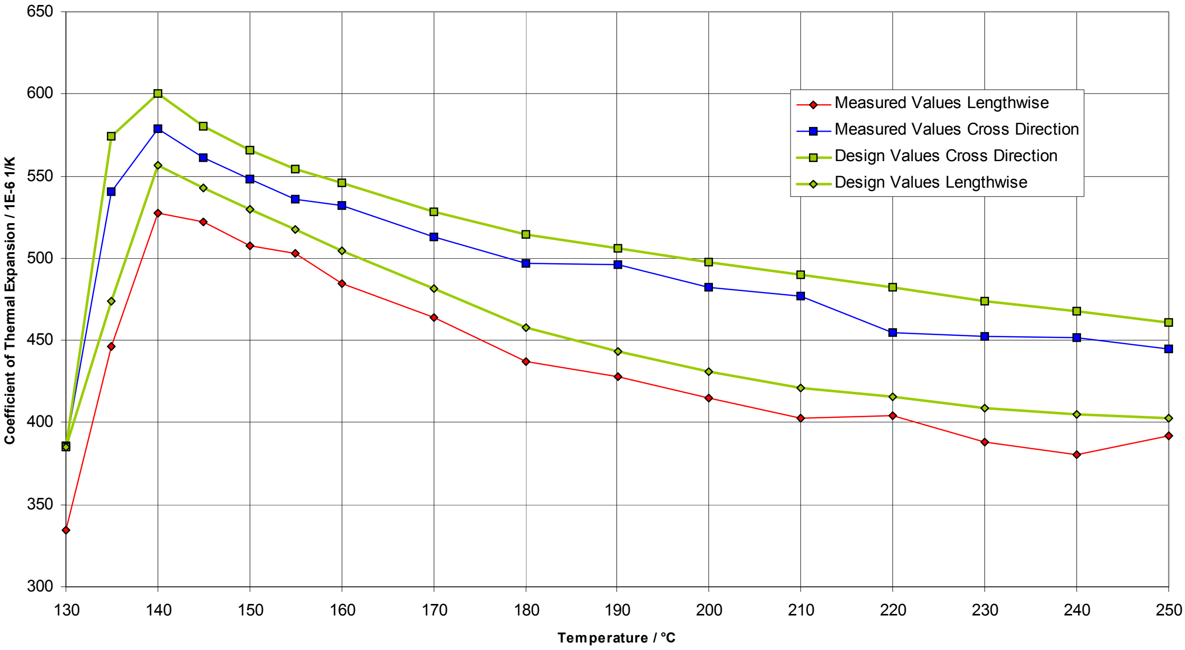

Fig. 2 Coefficients of thermal expansion as a function of temperature and direction

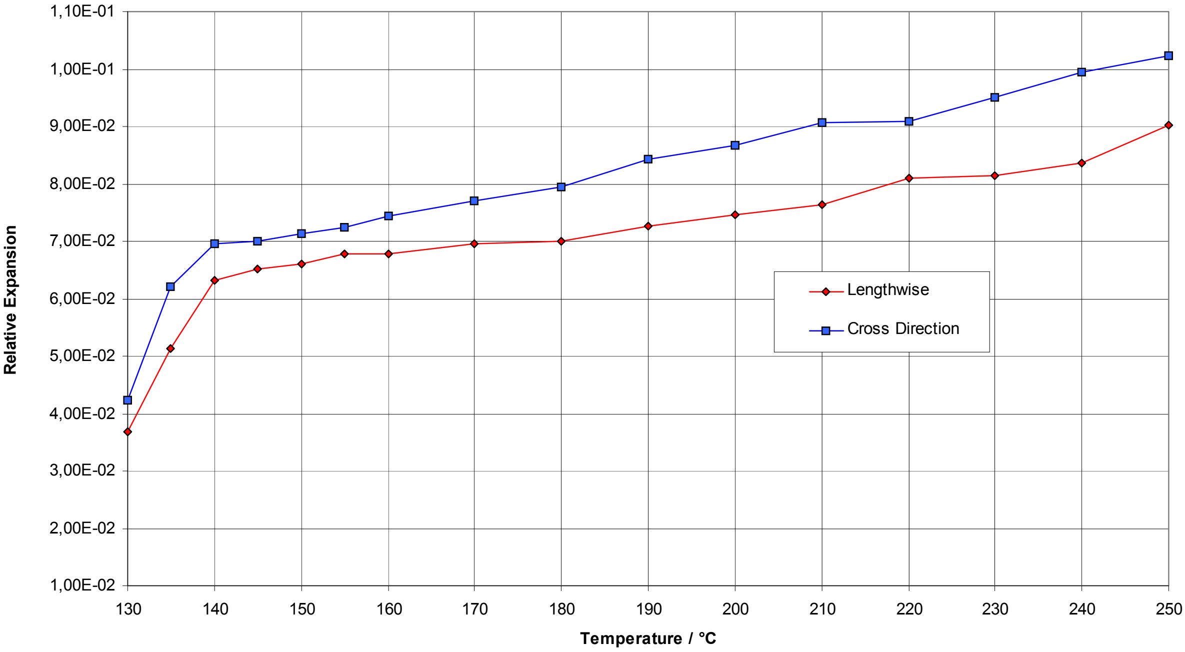

Fig. 3 Relative thermal expansion as a function of temperature and direction

temperature around 140 °C lengthwise with a value of $556 \cdot 10^{-6}$ K^{-1} and in cross direction with $600 \cdot 10^{-6}$ K^{-1}. For higher temperatures the measured coefficients decrease.

Figure 3 shows corresponding relative thermal expansions of round rods in temperature ranges between 130 °C and 250 °C. Relative expansions are strictly increasing over the whole range.

BAM assesses the shown coefficients of thermal expansion as sufficiently safe from a statistical point of view. The design values are expedient for the proof of the free expansion behaviour of UHMW-PE in CASTOR®-casks.

4. Thermal expansion behaviour towards multiple heating and cooling

Transport and storage casks of CASTOR®-design can be exposed to multiple heating and cooling processes because of possible repeated loadings and unloads of radioactive materials with heat generation. That is why BAM has to assess the influence of thermal cycles on the expansion behaviour of UHMW-PE. The applicant has to prove the behaviour and has to account for that in designing the cask. So GNB investigated the influence of thermal cycles on round rods of original size as well as under original assembling conditions in a cast iron pipe.

4.1. Investigation with round rods of original size

Round rods made of UHMW-PE in original size were subjected to three different test temperatures (130 °C, 140 °C and 160 °C) each with five temperature cycles including heating up to the test temperature and cooling down to standard ambient temperature. New round rods were used at each test temperature.

Figure 4 shows relative lengths of round rods after cyclic heating and cooling based on initial length. At all three test temperatures the expansion during the first heating is larger than the following ones. This behaviour is more significant at the test temperature of 130 °C, below the melting temperature of crystallites than at the other ones above. Generally, at test temperatures above the melting temperature the behaviour of thermal expansion of round rods is more consistent. Round rods cooled from 130 °C show partly a smaller length than the initial length. This is not the case after heating up to 140 or 160°C and cooling. There was no contraction of the cold samples compared to the initial ones.

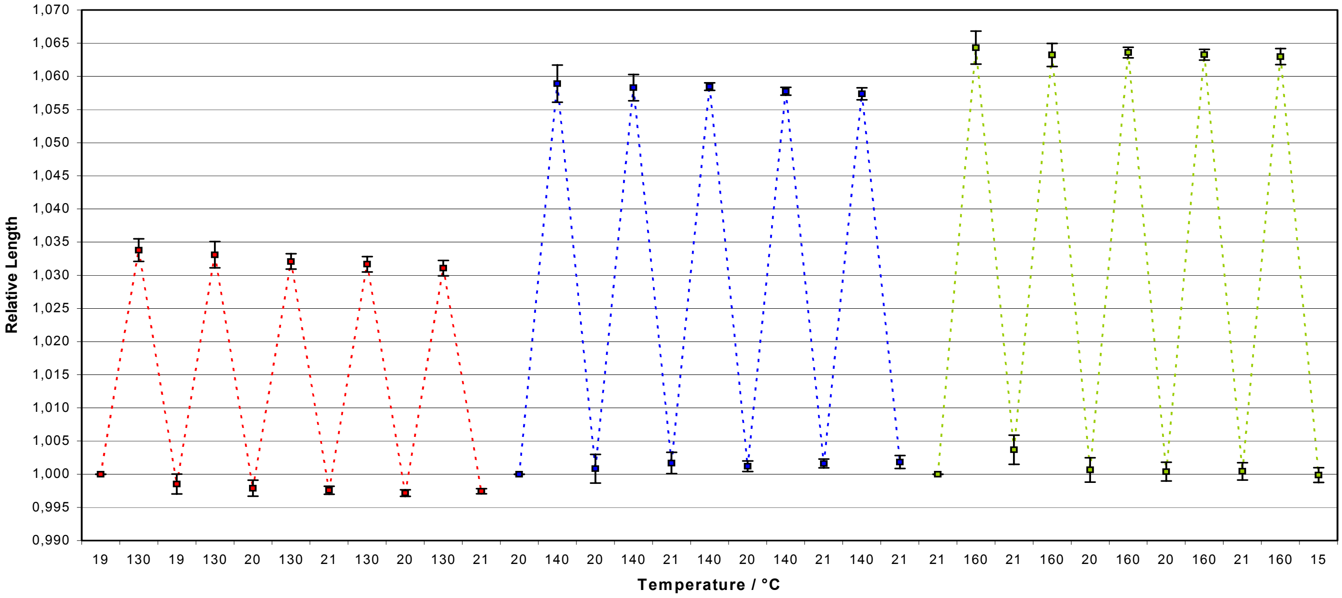

Fig. 4 Relative lengths of round rods after cyclic heating and cooling

Figure 5 shows relative diameters of round rods after cyclic heating and cooling based on initial length. Similar to relative lengths, a reduction of diameters on heating during the cycles is shown. However, relative diameters do not decrease monotonously from cycle to cycle, but show an increase in length on heating at some cycles: at 130 °C from 1st to 2nd cycle, at 140 °C from 4th to 5th cycle and at 160 °C from 2nd to 3rd and from 4th to 5th cycle. This behaviour is still more distinct in a cold state. But the diameter of the cold rods is not smaller than the original diameter. The increases in diameters in a cold state related to the original length are higher for test temperatures above the melting temperatures of crystallites than for the temperatures below it.

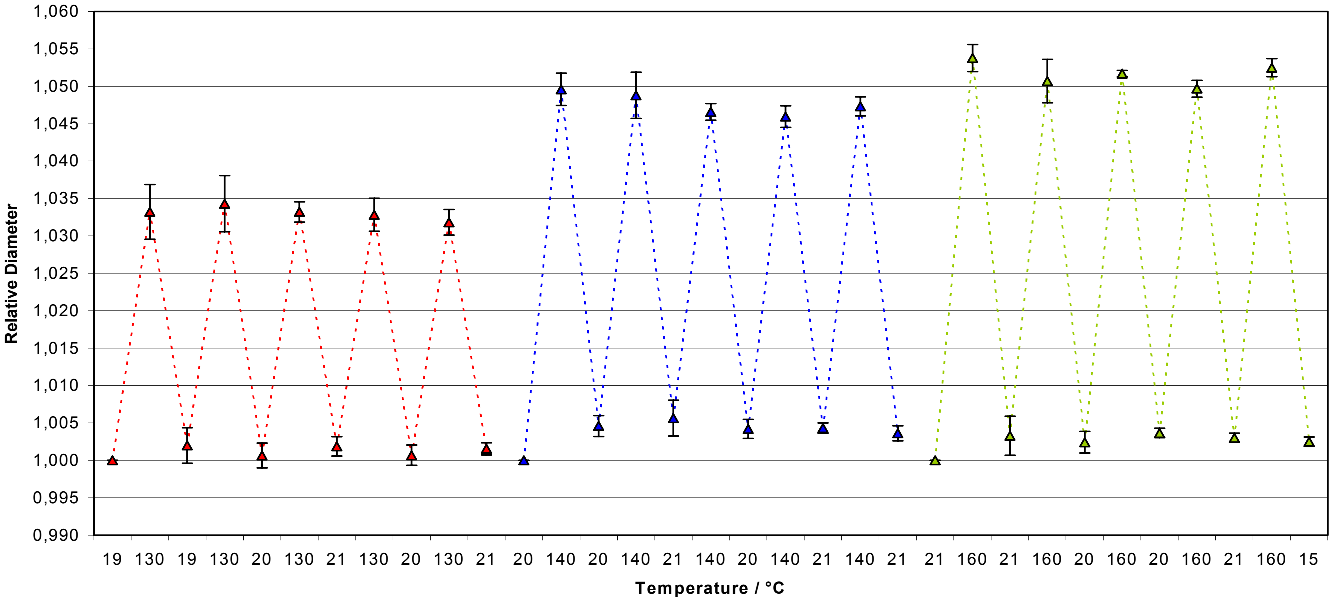

Fig. 5 Relative diameters of round rods after cyclic heating and cooling

BAM assesses the geometrical changes in relative lengths and diameters either in the cold or in the heated state over all the cycles as relatively small. The expansion behaviour is reproducible in the limits of measurement errors and in the limits of the known behaviour of the UHMW-PE. The results do not show any behaviour that could indicate any special unexpected changes in materials structure.

4.2. Investigation in a cast iron pipe

Round rods made of UHMW-PE were investigated in a cast iron pipe, see figure 6, under real assembly conditions concerning geometry and cyclic temperature and pressure loadings. It was the aim to realize possible global geometrical changes on neutron moderator columns in the CASTOR®-casks. This includes, besides the mentioned expansion behaviour, also possible boundings of round rods on each other or on the wall of the bore holes, the generation of gaps between single round rods of the moderator column or changes from round to oval shapes of the rods. These geometrical changes have to be assessed by BAM with respect to the usability of UHMW-PE for higher temperatures in transport and storage casks of CASTOR®-design.

Fig. 6 Cast iron pipe with bore

holes, heater mats and instrumentation
GNB arranged a large scale experiment with two neutron moderator columns, see figure 7, in holes of the cast iron pipe. Each column consisting of several round rods was mechanically loaded by a spring and thermally loaded by three successive heating-ups to a temperature of 160 °C and cooling downs to standard ambient temperature. The dwell time for each heated stage was at least 50 hours. Figure 8 shows percentile changes of length of neutron moderator columns together with the respective temperatures as a function of measurement numbers.

In principle the shown expansion behaviour of the neutron moderator columns during the heating can be calculated within the error limits of the results. Models were developed, depending on initial length, temperatures and thermal expansion coefficients from section 3. However, calculated length expansions are higher than the measured ones. The elastic properties of UHMW-PE, especially at temperatures above the melting temperature of crystallites, result in an additional rearrangement of length expansion into diameter expansion. This rearrangement was also confirmed by calculation.

While cooling down the neutron moderator columns, the rearrangement effect in combination with the lengthwise mechanical load by the spring partly leads to contractions of the columns at standard ambient temperatures. In conjunction the diameter of the cold round rods becomes larger after heating cycles.

Fig. 7 Moderator column consisting of several rods

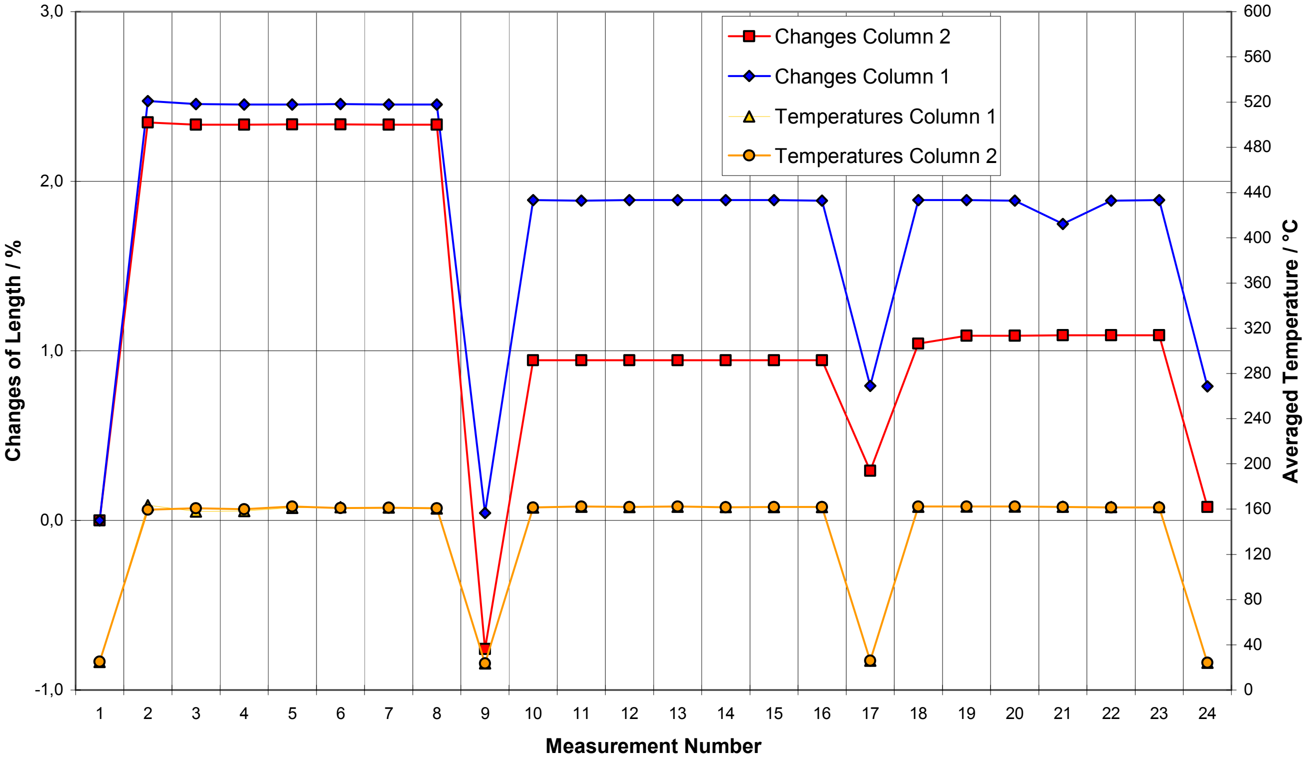

Fig. 8 Changes in the length of neutron moderator columns and temperatures

Because of the lengthwise mechanical load of the moderator column the single round rods were bounded together at their face-side. By that it can be ensured that the moderator column is without gaps between the single rods of the column.

Some oval shapes in rods were found by visual inspection after disassembling the moderator column when the investigation was finished. The oval shapes were bounded locally. The maximum change in diameter was ± 2 % of the round diameter.

BAM is of the opinion that the proof is given by these cast iron pipe investigations that the behaviour of the moderator columns does not differ fundamentally from the known behaviour. An exception is the elastic rearrangement of lengthwise expansion to cross direction that can be followed by calculation and that has to be taken into account in designing the moderator columns in original casks. Such effects of glue leading to undefined gaps between moderator rods were not found. The oval shapes from these investigations are not relevant for the safety of application in transport and storage casks of CASTOR®-design.

5. Creep behaviour of samples under constant pressure load

Mechanical loads, brought up by compressed springs in bore holes of CASTOR®-casks, influence the creep behaviour of moderator columns. It is well known, that thermoplastics like UHMW-PE show creep behaviour under mechanical load. To investigate creep behaviour of UHMW-PE under constant pressure load, samples were subjected to two different pressure loads at a temperature of 160 °C in a furnace during a time of 4500 hours. After well defined time steps, the length of the samples were measured and the degree of compression was calculated.

Figure 9 shows the creep compression as a function of annealing time during 4500 hours of annealing for samples without mechanical load as well as loaded with pressures of 0.05 MPa and 0.15 MPa. A pressure of 0.05 MPa generates a maximum confidence creep compression of 2.7 % and a pressure of 0.15 MPa generates 9.8 %. An extrapolation of measured compressions with respect to 95 % confidence interval up to an annealing time of 40 years, gives a maximum creep compression of 2.7 % at 0.05 MPa pressure and of 12.1 % at 0.15 MPa.

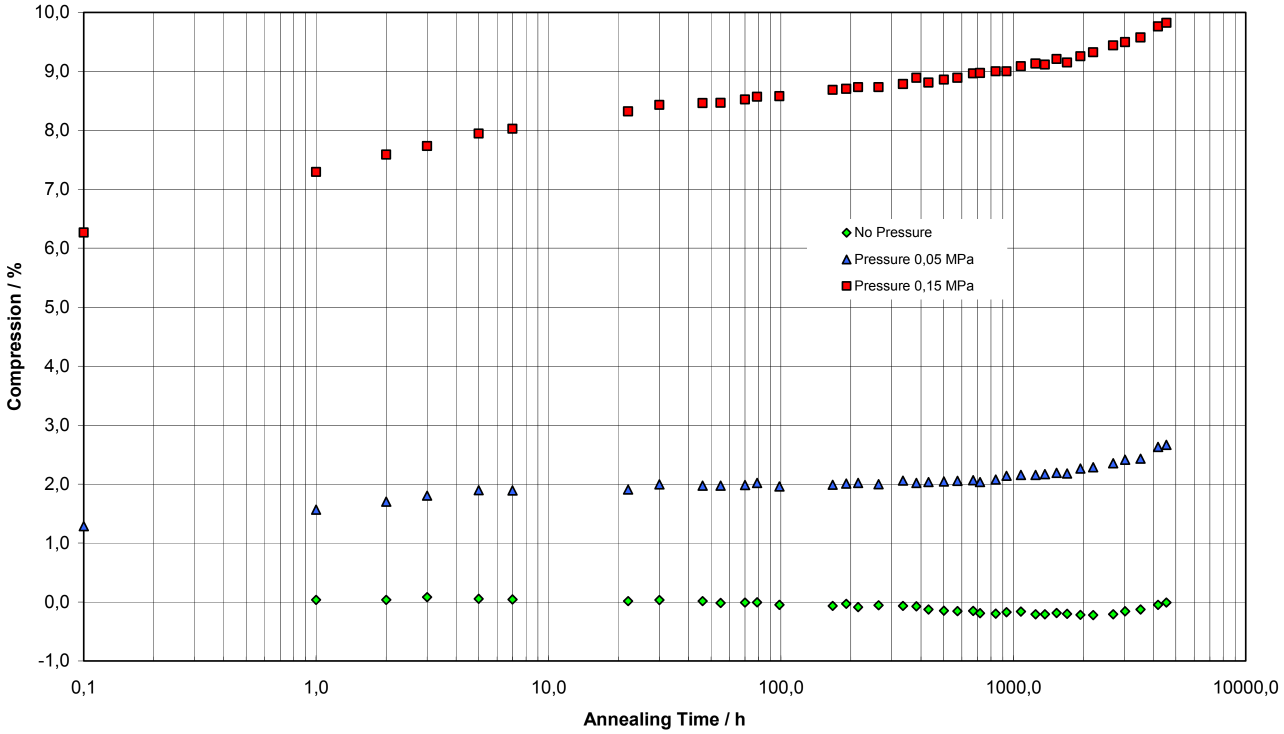

Fig. 9 Creep compression as a function of annealing time during 4500 hours of annealing

BAM assesses, that the creep behaviour has to be taken into account in designing moderator rods and springs in the bore holes of CASTOR®-casks. This has been done by GNB for temperatures up to 130 °C and must be calculated for the maximum temperature of 160°C, too.

6. Exhalation under thermal load

To assess the influence of high temperatures on the chemical and physical structural properties of UHMW-PE, the exhalation from samples was investigated. For that, samples surrounded by air, by air-argon and by nitrogen were included into flasks. The samples were heated to a temperature of 170 °C with an annealing time of 3000 hours. After fixed times the samples were inspected visually, the composition of gas inside the flasks was measured and its components were quantified.

During the annealing time, all samples had a temperature of 170 °C and were in an amorphous state. There were no visible changes of the geometrical shapes of the samples. After cooling and re-crystallisation, samples partly showed a change, from their white colour to a slightly yellow one. The change depended on the time in the heated flask and on the availability of oxygen inside the flask. The samples in pure nitrogen atmosphere had no discolouration. The surface structure of the cooled samples after the thermal load looked like the samples before.

By gas chromatography after annealing time the existence of the molecules H_2, O_2, N_2, CO, CO_2, CH_4 and C_2H_6 in the flask atmosphere was analysed. Figure 10 shows the volumes of hydrogen in dependency of the annealing time of heating. A functional dependency of gas volumes on annealing time is not visible. The volume of hydrogen had a maximum of 0.039 ml_N under air atmosphere, compared to lower volumes under air-argon atmosphere 0.010 ml_N and under nitrogen atmosphere 0.007 ml_N.

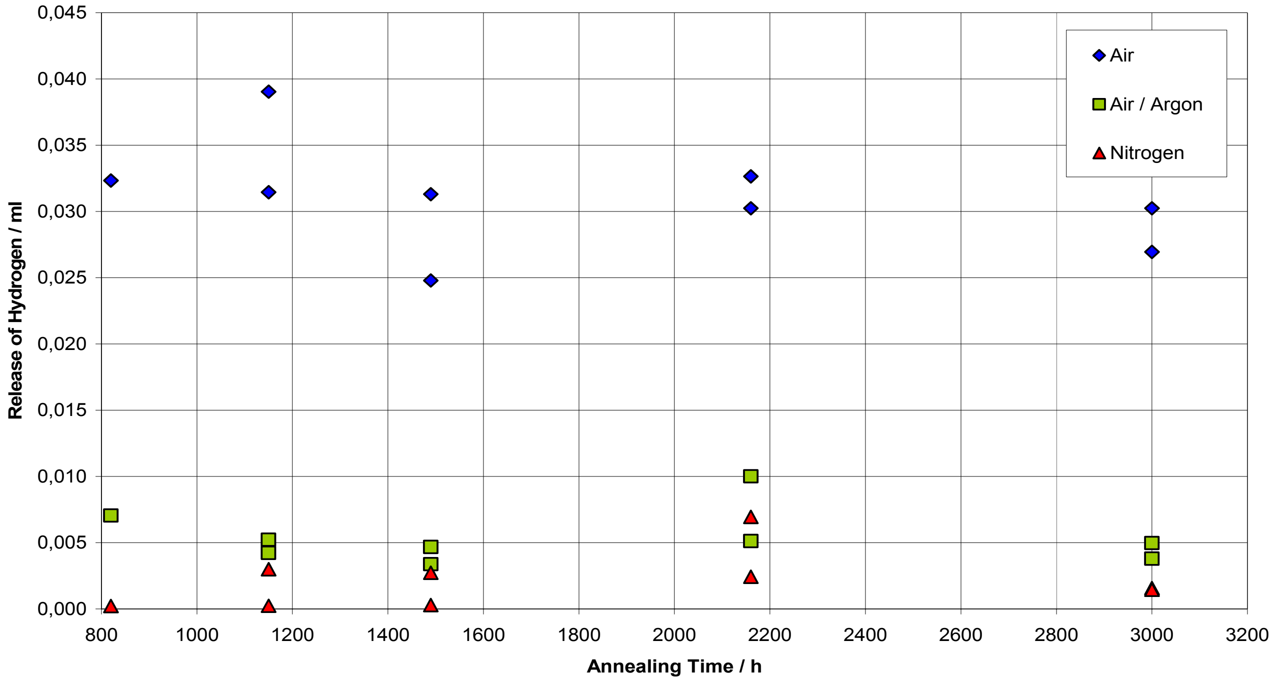

Fig. 10 Hydrogen release in dependency of annealing time

The gas volumes of CO and CO_2 do not depend visibly on the gas atmosphere (air, air-argon, nitrogen) in the cask. The volumes of CH_4 and C_2H_6 are below the limit of detection. The initial volumes of O_2 in air and air-argon atmospheres were used for sample surface oxidation processes.

BAM is of the opinion that the gas production was very small for all samples. The maximum volume 0.039 ml_N reached hydrogen under air atmosphere at an annealing time of 1150 hours. The theoretically releasable volume of hydrogen for those samples is near 15 l. Thus, the produced gas has 0.00026 % of the theoretical value. The gas production is negligible in air atmosphere. With reduced air or without air atmosphere it is smaller again and also negligible.

7. Chemical and physical structural properties

Samples subjected to mechanical and thermal loadings as described in section 6 were investigated as well as samples without such loadings. These samples were subjected to analytical methods like CH-Elemental Analysis (CEA) and Differential Scanning Calorimetry (DSC).

By CEA, the concentration of carbon and hydrogen inside the samples was analysed. Results give indications of possible changes inside the materials of the samples, especially about their properties as neutron moderation materials. With respect to the unloaded samples with 13.68 % of hydrogen concentration, there was a mean reduction in loaded samples near 0.51 % under nitrogen atmosphere and near 0.1 % under air-argon atmosphere. Under air atmosphere, there was a 0.1 % higher concentration of hydrogen. The results of carbon concentration gave mean reductions of 0.02 % and 0.03 % and in the case of nitrogen atmosphere there was an increase in carbon concentration.

BAM is of the opinion that the results of CEA show only very small changes in the concentration of carbon and hydrogen under mechanical and thermal loads, investigated for all samples. These changes are negligible concerning the properties of neutron moderation of carbon and hydrogen in UHMW-PE.

By DSC, the melting behaviour of the materials of the samples was analysed. Results can give proof of structural changes in the degree of crystallinity, in enthalpy or in the peak transition temperature. As expected, the results of unloaded samples show such changes between the 1st and the 2nd melting. This differs from the behaviour of the long time heated samples. They do not show such a difference between 1st and 2nd melting. For 2nd melting the results of the unloaded and loaded samples agree with respect to the precision of the method. There was also no significant difference in the results between samples under air, air-argon and nitrogen atmosphere.

BAM agrees with results from DSC-analysis. No significant structural changes could be identified in long term heated samples, in comparison with non-heated samples. The results agree with that for usual UHMW-PE according to materials specification.

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