

## Three-dimensional thermal expansion of neat and irradiated (U)HMWPE materials at elevated temperatures

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### ABSTRACT

The thermal expansion of polymeric parts can be an issue in many applications where the available space is limited, or exact dimensions of the part are required. For this study, a device was designed and built that allowed measuring the thermal expansion simultaneously in all three spatial directions on cubic samples with real-scale dimensions (78 mm edge length). The results are shown between 25 °C and 125 °C for two PE materials, one HMWPE and one tempered UHMWPE, for non-irradiated samples as well as cubes that have been irradiated with 100 and 400 kGy. The results measured with the new device were very similar to those measured with conventional thermo-mechanical analysis equipment and to literature data of UHMWPE. The HMWPE material shows a much larger thermal expansion coefficient in one direction compared to the other two directions during the first heating due to frozen stresses from the pressing step during material manufacturing. These stresses are mostly released by the expansion during the first heating, so that the expansion during the second heating is more uniform. The overall volumetric expansion is the same for both heating runs. By contrast, the tempered UHMWPE material shows no significant difference between first and second heating run, as the stresses from processing could already relax in the tempering step. The irradiation treatment does not affect the values significantly for the given test set-up.

### 1. Introduction

Polyethylenes (PE) with high molecular weight (HMWPE) or ultra-high molecular weight (UHMWPE) have special properties such as good impact strength, abrasion resistance and chemical stability [1]. Therefore, they are used e.g. as slide bearing or in medicine as joint replacements [2]. Because of their high hydrogen content, they are also used as neutron radiation shielding materials in casks for transport and/or storage of radioactive material [3,4]. In such casks, PE rods are positioned in boreholes within the cask wall and PE discs in the top and bottom of the cask. In this application, the materials are exposed to elevated temperatures and high gamma and neutron radiation rates over long time periods caused by the radioactive inventory of the cask. The effects of temperature and radiation on the chemical structure, morphology and mechanical properties of these materials have been investigated by us previously [5,6]. Irradiation of UHMWPE in medical applications is also common for sterilization or inducing additional crosslinking for property enhancement [7,8]. As the mounting position

of the neutron shielding materials within casks is spatially limited, the thermal expansion of the materials is of special interest for this application.

Thermo-mechanical analysis (TMA) measures the expansion or dilation of a material with increasing temperature. In polymers above the glass transition temperature, the thermal expansion is mostly correlated to the increase in free volume, while the actual volume of the molecules (“hard-core volume”) hardly changes [9]. As the free volume in the crystalline structures is limited, polymers with a lower degree of crystallinity expand more and exhibit a higher coefficient of thermal expansion (CTE) [10]. The CTE increases with increasing temperature, which becomes especially pronounced when the melting starts in semicrystalline polymers such as PE. While the polymer chains had been space-savily folded in the crystalline state, they unfold during melting and occupy a much larger space in the amorphous molten state. As crystals in semicrystalline polymers have very different sizes, the melting point is not a sharp transition, but a broad range, with smaller crystals melting already at lower temperatures. The coefficient of linear

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thermal expansion corresponds to the slope of the elongation/temperature curve. For a limited temperature range in which CTE is practically constant, it can be determined by dividing the measured expansion (normalized to the original length) by the corresponding temperature difference.

The thermal expansion behavior of the above mentioned PE materials in dependence of temperature and radiation dose has not been investigated in detail previously. Conventional one-dimensional thermo-mechanical analysis (TMA) on cubic samples with 4 mm or 6 mm edge length can yield continuous information on the thermal expansion. However, this method may not be very well suitable for assessing the thermal expansion of the large-scale PE components as used e.g. in casks for radioactive waste, as e.g. Pastine et al. [11] have shown that the thermal expansion coefficient depends on the sample volume. Additionally, conventional TMA does not take into account possible differences between the three spatial dimensions. Therefore, obtaining information for different directions would require measurements on several samples. Directional differences have been described in literature especially for oriented PE [12,13], but can also originate in other fabrication processes such as compression molding [14].

Studies on thermal expansion of PE found in literature focus on temperature ranges up to 300–350 K (77 °C) as maximum (e.g. Refs. [13, 15]). However, for some applications, as e.g. in casks for radioactive waste, higher temperatures are relevant. Therefore, this study takes into account temperatures up to 125 °C, at which point significant melting starts as determined with Differential Scanning Calorimetry.

To sum up, literature relevant to this material and application conditions is scarce and detailed investigations are necessary. For this reason, a device was designed and built that allowed measuring the thermal expansion at elevated temperatures (from ambient to 125 °C) simultaneously in all three spatial directions on cubic samples with 78 mm edge length. The results are shown for two PE materials, a HMWPE and a tempered UHMWPE, for non-irradiated samples as well as cubes that have been irradiated with a gamma( $\gamma$ ) dose of 100 and 400 kGy.

## 2. Experimental

### 2.1. Materials

The analyzed linear UHMWPE material is a tempered GUR 4120 from Ticona (Celanese) with a molecular weight of about 5 million g/mol, which is more than ten times higher than that of HMWPEs. The HMWPE used in this study is a high-density Lupolen 5261 Z from Lyondell Basell. The polymers were processed by compression molding into blocks that were cut into cubes with 78 mm edge length. The samples were named by four parameters according to the scheme in Table 1, e.g. L1\_2\_B or G400\_1\_C. The first letter is the abbreviation for the material, the following number corresponds either to the sample number (for unirradiated samples) or to the irradiation dose (for irradiated samples), the next number names the heating cycle and the last letter indicates the measurement direction which applies only to samples measured with the new device.

The samples were irradiated under air at ambient conditions with a  $^{60}\text{Co}$  gamma source by Synergy Health Radeberg GmbH, Germany, with an average dose rate of approximately 3 kGy/h.

Fig. 1 shows Differential Scanning Calorimetry (DSC) curves during the first heating of 10 mg samples of the materials heated with 10 K/min

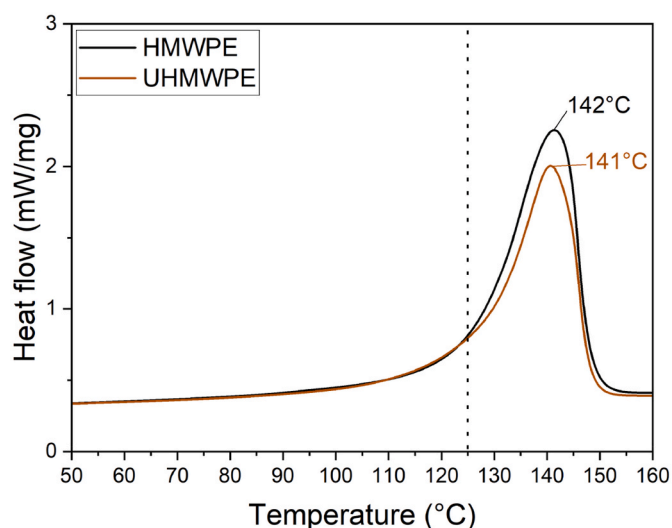


Fig. 1. DSC curves of HMWPE and UHMWPE in the first heating with melting peak temperatures. The highest thermal expansion test temperature is marked by the dotted vertical line at 125 °C.

under nitrogen in a Netzsch DSC 204 F1 Phoenix. The maximum of the melting peak is at 141 °C for UHMWPE and at 142 °C for HMWPE, indicating a similar average crystal size [9]. On the other hand, the degree of crystallinity (corresponding to the peak area [16]) is higher for HMWPE (63%) as compared to Gur (56%), as the HMWPE chains are shorter and therefore have more mobility for crystallization.

### 2.2. Measuring device

The device that was designed for the specific purpose of measuring the thermal expansion simultaneously in all three spatial directions on real-scale samples is shown in Fig. 2. It consists of a base plate and two walls (yellow) that allow precise positioning of the cubic samples (green). The device and the sample were placed in an air-circulating oven (Vötsch VT3) and heated up. The thermal expansion was measured in all three directions with the respective elongation sensors (red). The sensors are fixed with clamps (blue) to the base plate or the wall, respectively. All parts are made of X5CrNi18-10 stainless steel with known thermal expansion behavior. The elongation sensors from HBM are able to measure both expansion and shrinkage of the samples, as a spring force of 3.6 N ensures contact to the sample during shrinkage. The net measurable range is up to 10 mm for two sensors of type WA10 and 20 mm for sensor type WA20, as this sensor will also be used in other experiments with larger samples. The linearity error is  $\pm 0.2\%$  for each sensor. The temperature is measured using a Pt100 temperature probe (class A) by Omega that is fixed in contact with the PE sample (not shown in the figure). The elongation and temperature sensors were connected to a HBM QuantumX MX440B universal measurement amplifier and were exported using the HBM Catman software.

### 2.3. Determination of thermal expansion coefficients

Prior to the measurement, the sensors were brought in contact with

Table 1  
Sample nomenclature.

Position in name	1	2	3	4
Refers to	All	Unirradiated samples	Irradiated samples	All
Meaning	Lupolen (HMWPE)/ GUR (UHMWPE)	Sample no.	Irradiation dose in kGy	1st heating/ 2nd heating
Used character	L/G	1/2/3/4	100/400	1/2
				Samples measured with new device Spatial direction
				_A/B/C

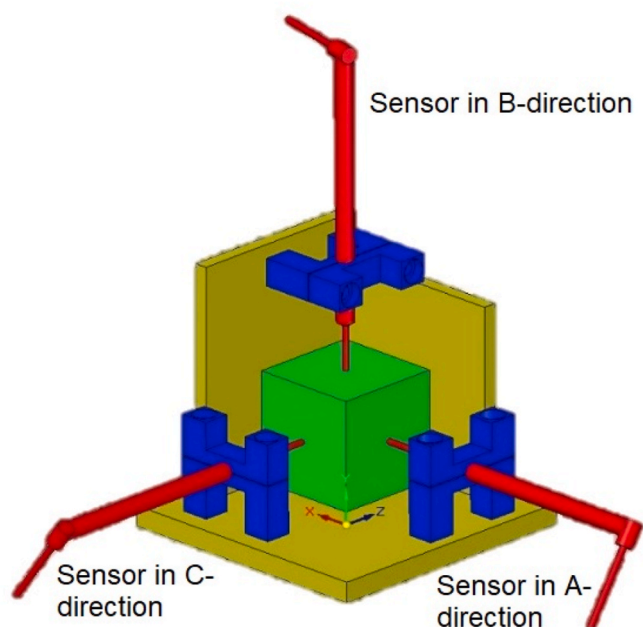


Fig. 2. Designed device for measuring the thermal expansion of 78 mm PE cubes (green) in three spatial directions. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the sample with a pre-compression of about 2 mm to avoid loss of contact to the sample during cooling and shrinking. The instrumented sample cubes in the measuring device were heated in 10 K steps from 25 °C to 125 °C.

After measuring the first heating of the first UHMWPE sample G1 and observing the steep rise of the CTE at higher temperatures, a temperature step at 120 °C was included for all further measurements to achieve a better resolution of this temperature region.

After the oven reached the specified temperature, it was necessary to hold the temperature for 5 h (25–85 °C), 8 h (95–105 °C) or 10 h (115–125 °C) respectively to reach thermal equilibrium and completion of thermal expansion of the sample for the specific temperature step. An increase of the holding time at the higher temperatures was necessary due to the beginning melting process. Measurement data were recorded every second. Fig. 3 shows the recorded sensor raw data for an

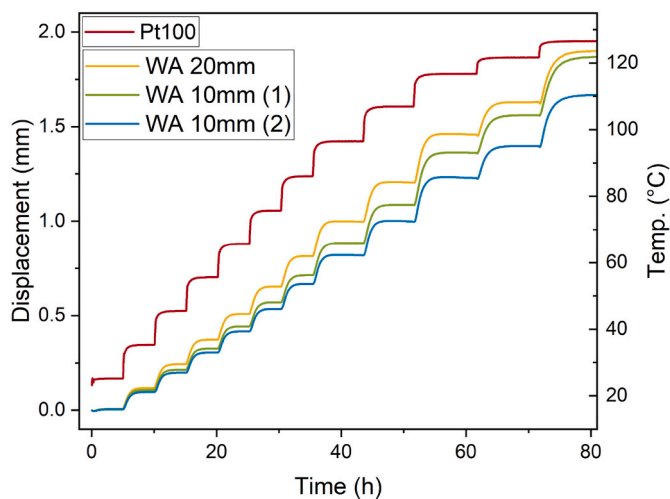


Fig. 3. Raw data of the elongation sensors (WA, left axis) and temperature sensor (Pt100, right axis) for a UHMWPE sample.

exemplary experiment. As the displacement lags behind the temperature steps due to the large samples, reaching thermal equilibrium takes considerable time. The peak displacement values of each temperature step are used for further evaluation of CTE.

The plateau value of the elongation sensor (designated respectively  $L_A$ ,  $L_B$  and  $L_C$  for each direction) was noted and corrected using a correction summand determined beforehand from a measurement on a stainless steel cube with known thermal expansion coefficient that had been heated with the same program. This compensates measurement errors resulting from the thermal expansion of the device itself as well as systematic and temperature-dependent deviations of the sensors. Then the thermal expansion coefficient CTE was determined for each direction by dividing the displacement difference in each temperature interval by the temperature difference and the sample length at the start of the temperature interval, as shown below.

$$CTE(T_{n+1}, T_n) = (L(T_{n+1}) - L(T_n)) / ((T_{n+1} - T_n) \cdot (L_0 + L(T_n)))$$

The resulting CTE was assigned to the average temperature of the measurement step, for example, 60 °C when CTE was determined between 55 °C ( $T_n$ ) and 65 °C ( $T_{n+1}$ ).

$L_0$ , the initial length, was measured in each direction prior to each heating run except for the unirradiated samples and the first heating of the UHMWPE sample irradiated with 100 kGy, as these were the first samples and the measurement procedure was not yet fully established. As we had only a very limited number of samples (two unirradiated and one irradiated for each dose and material), measurements could not be repeated at will. Therefore, an  $L_0$  of 78 mm was assumed for these samples. Generally,  $L_0$  of neat samples laid between 78 and 78.11 mm, and  $L_0$  of samples after the first heating and cooling laid in the same range for the tempered UHMWPE and between 76.79 mm (A and B direction) and 80.47 mm (C direction) for the HMWPE. Accordingly, the measurements of the mentioned UHMWPE samples and of the first heating of neat HMWPE samples can include a negligible error of about 0.1%, and the neat HMWPE measurements can include an error of up to +1.6% (A and B direction) and –3.1% (C direction) for the second heating.

After holding the final temperature for the specified time, the oven was cooled down again to 25 °C.

#### 2.4. Conventional TMA

The conventional TMA was conducted on cubes with 6 mm edge length using a Seiko Instruments TMA/SS120C device. After measuring  $L_0$  at room temperature, the UHMWPE samples were cooled to –70 °C with a cooling rate of 10 K/min, then heated to 200 °C with 2 °C/min, cooled again to –70 °C with 2 °C/min, and heated a second time to 220 °C with 2 °C/min with nitrogen purging throughout. For the HMWPE, the first heating was performed only up to 145 °C as the melting material softened above this temperature. In order to be able to compare the results to the ones measured with the new device, the displacement values for the same temperature steps were extracted (e.g. for 25 °C, 35 °C etc.) and evaluated as described above.

### 3. Results & discussion

#### 3.1. HMWPE

The measured coefficients of thermal expansion (CTE) for the three spatial directions are shown in Fig. 4 for two different HMWPE samples during (a) first and (b) second heating. The second heating shows the usual behavior for thermoplastic, semi-crystalline materials, as the CTE is almost constant and increases slowly at lower temperatures, but faster at higher temperatures when melting starts. On the other hand, during the first heating, CTE in C-direction increases considerably with temperature, while CTE(A) and CTE(B) are much lower and decrease

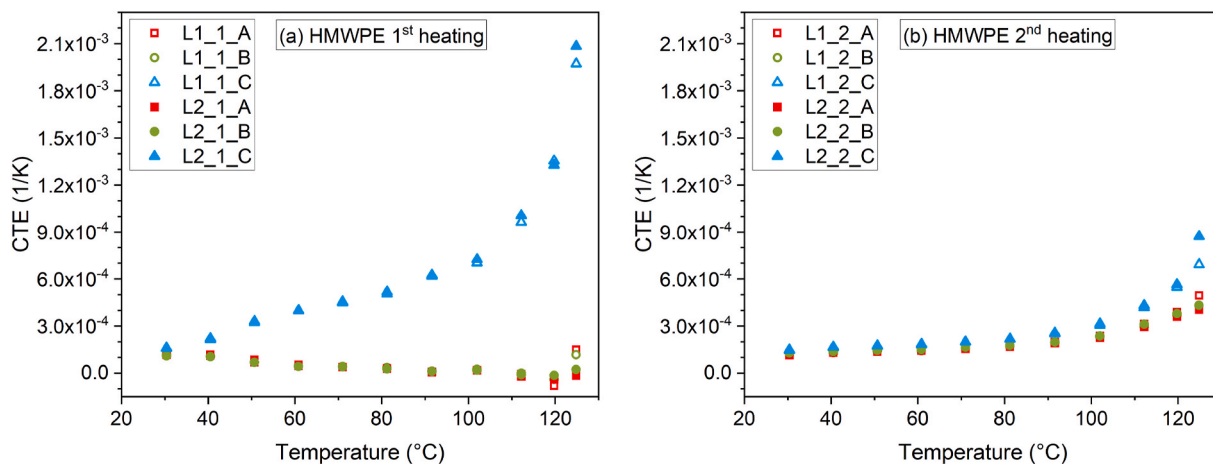


Fig. 4. Coefficient of thermal expansion (CTE) of two different HMWPE samples (L1 and L2) during (a) first heating and (b) second heating in the three spatial directions A, B and C. Sample 1 is represented by open symbols, sample 2 by full symbols.

slightly over temperature, reaching approx. Zero around 100 °C. These large differences between the directions originate in the fabrication process of the cubes, during which the HMWPE granules are molded into plates at elevated temperatures and are cooled in this form under pressure. Afterwards, smaller blocks are sawed from the larger ones. Thus, direction C corresponds to the pressing direction during fabrication, and the other two directions lie perpendicularly in the plane of the rectangular plate. During cooling under pressure, stresses are frozen in the material and are responsible for the different expansion behavior in different directions. This is observed as a more pronounced elongation in C direction and a smaller thermal expansion or even shrinkage in directions A and B. This anisotropy is already clearly observable after 30 K temperature increase. During the first heating process, most of the frozen stresses can relax. As the cooling step after the first heating is performed rather slowly and in a stress-free condition, the expansion is much more uniform during the second heating, although a slightly higher expansion in C direction is still observed. A similar effect based on the same mechanism has been described for oriented PE [12,13]. In the second heating run with uniform values, the CTE lies between 1 and 11 × 10<sup>-4</sup> 1/K, while it reaches values up to 21 × 10<sup>-4</sup> 1/K in one direction in the first heating and even slightly negative values in the other directions. Negative CTEs can be caused by rubber-elastic contractions of taut tie-molecules [17]. Thus, the measured negative CTEs originate in the material processing history and are not an intrinsic material property. In the range up to 80 °C often covered in literature, the values

in Fig. 4(b) are typical for (U)HMWPEs with around 1–2 × 10<sup>-4</sup> 1/K [2].

It can also be seen that the values for the two samples lie very close together, demonstrating the good reproducibility of the measurement.

For comparison, the CTE values determined using conventional TMA are displayed in Fig. 5 together with the data of the large sample L2. Even though four different samples were measured, none displayed the pronounced thermal expansion in C direction that was observed on the large cubes. This indicates that this direction was missed, as it is hard to keep track of the sample orientation during several successive sawing and cutting steps that are necessary to obtain the small cubes for TMA measurements from the large blocks supplied by the manufacturer. This illustrates the advantage of being able to measure all three spatial directions simultaneously on one large block. Even though the steep rise could not be directly compared, the other available data show a very good overlap between the two methods, validating our test set-up. Unfortunately, no additional TMA measurement could be made for this paper, as the original measurements were performed several years earlier, and the TMA device is no longer in service.

Fig. 6(a) shows the coefficient of thermal expansion (CTE) averaged over the three spatial directions for the two different HMWPE samples during first and second heating determined with the new device. Again, the overlap between the two samples is very good. The increase of CTE is moderate up to about 100 °C and rises more steeply at higher temperatures, when more crystals start to melt and lead to a stronger volume expansion. For the temperature range up to 120 °C, no difference

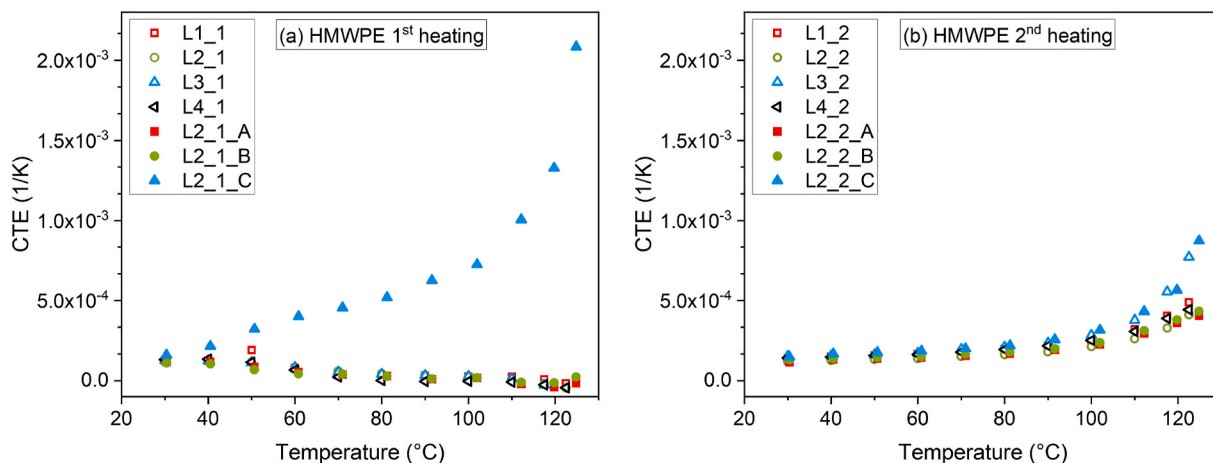


Fig. 5. Coefficient of thermal expansion (CTE) of HMWPE samples measured using conventional TMA (open symbols) and in different directions using the new device (full symbols, sample L2) during (a) first heating and (b) second heating.

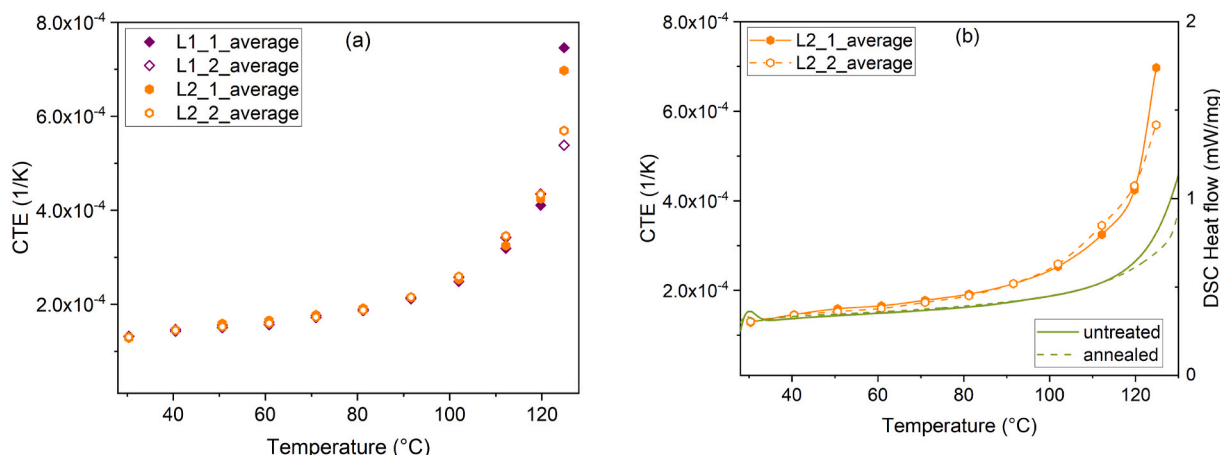


Fig. 6. Coefficient of thermal expansion (CTE), averaged over the three spatial directions for (a) two different HMWPE samples and (b) HMWPE sample L2 and DSC curves for untreated and annealed samples. The first heating/untreated sample is represented by a smooth line, the second heating/annealed sample by a broken line.

between first and second heating can be observed, indicating that the overall volumetric expansion in this temperature range is the same during both heating runs. At the highest investigated temperature range (120–125 °C), the samples exhibit a higher expansion in the first run compared to the second. This can be explained as follows: During the first heating of the CTE measurement with the new device, the sample is only heated to 125 °C (below the melting peak) and held there. At this temperature, the melting of the smallest crystals has just begun (cf. Fig. 1). By slowly heating to 125 °C and holding this temperature for relatively long times, the first heating run acts as an annealing step promoting crystal growth of crystals with melting points near 125 °C. This was confirmed by DSC measurements with a first heating run that simulated the thermal treatment of the large samples during the first heating of the CTE measurement according to the following program:

- Slow heating with 1 K/min up to 125 °C
- One hour isotherm at 125 °C
- Slow cooling with 1 K/min down to 100 °C
- Normal cooling with 10 K/min down to 25 °C
- Normal heating with 10 K/min up to 130 °C for comparison with standard DSC measurements (see Fig. 1)

By plotting together DSC curves of the first heating under standard conditions and of the second heating after the annealing step as first heating, the influence of the annealing step can be assessed as shown in

Fig. 6(b). Due to the crystal growth in the annealing step/first heating, melting starts at a higher temperature in the second heating run compared to the first heating run (of standard DSC measurements). Thus, the CTE and DSC curves of the second heating show a lower increase above 120 °C compared to the first heating. Additionally, differences between first and second heating can be due to different cooling conditions after manufacturing and after the first heating of the CTE measurement, which would lead to differences in crystal formation and thus in the melting peak.

Fig. 7 shows CTE of samples without irradiation treatment and with irradiation of 100 and 400 kGy, respectively of HMWPE, both for the first (a) and second (b) heating run. The HMWPE sample L2 was chosen as unirradiated reference. Generally, the irradiation treatment does not influence the values significantly. The only small effect that can be observed is a slightly lower CTE in C direction in the first heating run (at temperatures up to 100 °C) as a result of irradiation, and a slightly higher CTE(C) in the second heating run. A possible explanation for this are crosslinking reactions (that have been described previously for irradiated HMWPE [5]) that may fix the stressed chains. Thus, these additional crosslinks can prevent the full expansion in the first heating run as well as the full decrease of the values in the second heating. However, it is possible that a larger effect of radiation could be observed in samples with a higher surface to bulk ratio during irradiation, as oxygen access is better in such thin samples [18]. Thus, in thin samples (as often used in related studies [2]), a higher amount of permanent

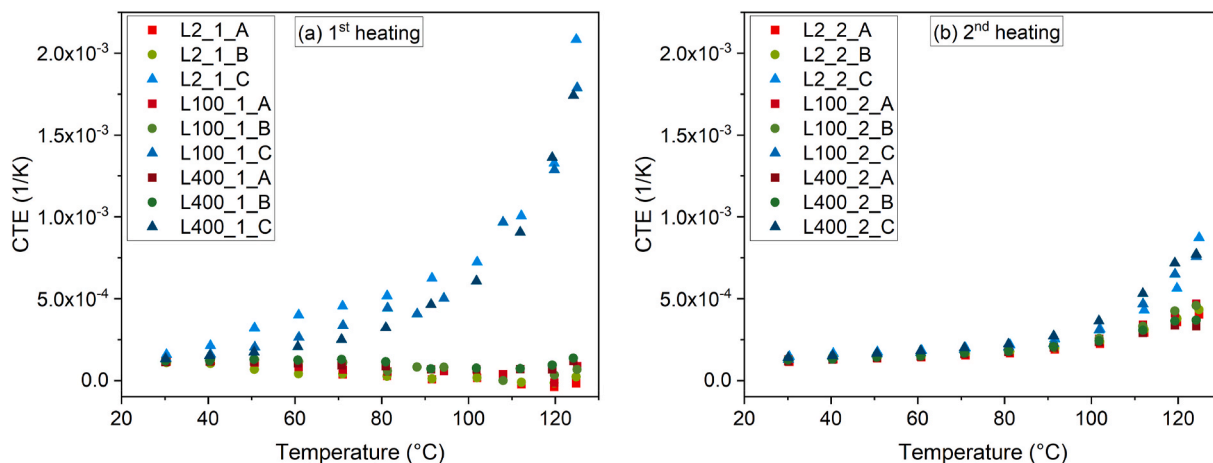


Fig. 7. Coefficient of thermal expansion (CTE) of neat and irradiated HMWPE samples during (a) first heating and (b) second heating in the three spatial directions A, B and C.

oxidation effects could occur via crosslinking and chain scission reactions, resulting in a higher influence of irradiation on microstructure and thermal properties than observed in the large samples of this study.

### 3.2. UHMWPE

The same measurements are now shown for the UHMWPE material. As the sample G1 was not heated to the additional temperature 120 °C in the first heating run (cf. Experimental section), the data points for the last three temperature steps do not represent the same temperature ranges (115 °C–125 °C for G1; 115 °C–120 °C and 120 °C–125 °C for G2). The additional temperature step for G2 allows a higher resolution of the temperature dependency of CTE.

Fig. 8 shows the CTE in all three directions for two different UHMWPE samples and both heating runs. The two samples yield similar results. As the UHMWPE material was tempered during manufacturing, the frozen stresses from processing could already relax to the most part. However, for temperatures higher than approx. 105 °C, a slightly higher increase of CTE is still observed in C direction, similar to the HMWPE material in the second heating. Apparently, the frozen stresses in the material could not relax completely in the tempering step during manufacturing.

Conventional TMA values for CTE and CTE determined with the new device are compared in Fig. 9. The values are similar, but slightly lower with conventional TMA during the first heating, and slightly higher during the second heating. The small differences could be due to the different sample dimensions as mentioned in the introduction. In the second heating, different results might also originate in the different maximum temperatures reached during the first heating, which is 200 °C (with complete melting) in the TMA measurements and up to 125 °C (only small crystallites start to melt) with the new device. As mentioned above, the TMA experiments were performed several years earlier and could not be adapted for more direct comparison to the experimental conditions with the new device. As discussed above for HMWPE and confirmed below for UHMWPE, the first heating acted as an annealing step promoting crystal growth of crystals with melting temperatures around 125 °C, thus leading to less melting and consequently lower thermal expansion in the second heating in the temperature range up to 125 °C, as observed in Fig. 9(b).

When comparing CTE averaged over all three directions, there are basically no differences between the two samples or the two heating runs for up to 110 °C, as can be seen in Fig. 10(a). Similar to the HMWPE, CTE increases more steeply for the highest temperatures due to melting crystals. This steeper increase is observed here for temperatures above 110 °C. This differs slightly from the temperature observed for HMWPE

(100 °C) due to the higher melting region of the crystals in UHMWPE [5]. Above 120 °C, CTE of UHMWPE is higher in the first heating compared to the second. This is in accordance with the DSC measurements that take into account the annealing function of the first heating during CTE measurements as discussed in the respective HMWPE section. Like the CTE data, the DSC curves display less melting in the temperature range of 120 °C–125 °C in the second heating as shown in Fig. 10(b). Furthermore, the UHMWPE material exhibits slightly higher average thermal expansion coefficients than the HMWPE material, which is probably due to the lower degree of crystallinity [10]. The measured values are in good agreement with that found in Ref. [2] for an UHMWPE with an average CTE of  $2.03 \times 10^{-4}$  1/K in the temperature range 32–110 °C.

The thermal expansion coefficients of non-irradiated UHMWPE (G2) and UHMWPE irradiated with 100 and 400 kGy are shown in Fig. 11 (a) for the first and (b) for the second heating run. No systematic differences can be observed, which means that the irradiation does not significantly affect the thermal expansion behavior of the UHMWPE in this temperature range. By contrast, Sreekanth et al. [2] observed a decrease of CTE by about 16% in the range between 50 °C and 80 °C after 100 kGy  $\gamma$ -irradiation which they attributed to additional crosslinking. In Ref. [2], the tested samples were disks with 2 mm thickness and 8 mm diameter. Even though  $\gamma$ -radiation can penetrate polymers very well, the large samples are possibly less affected than the thin disks due to lower oxygen access. Furthermore, the specific material formulation can influence the resistance to irradiation effects.

### 3.3. Advantages and disadvantages of the new test set-up compared to conventional TMA

When comparing the two test methods, the specialized conventional TMA device exhibits a better temperature and displacement resolution. Additionally, the samples are heated under nitrogen atmosphere in the TMA, which prevents degradation of the sample resulting from the high temperatures (up to 220 °C). However, as the (U)HMWPE samples are relatively stable [5,6] and were only heated to 125 °C in the new test set-up, the degradation resulting from the thermal treatment under air should be negligible. If necessary, an enclosure and nitrogen atmosphere could be realized as well in an advancement of the new device. One disadvantage of the new device are the long holding times that are necessary for reaching thermal equilibrium in the large samples and the accordingly long measurement times. However, this is compensated by the fact that one measurement covers all three directions, while three successive experiments are necessary with the conventional TMA. Measuring all three directions simultaneously is especially useful for

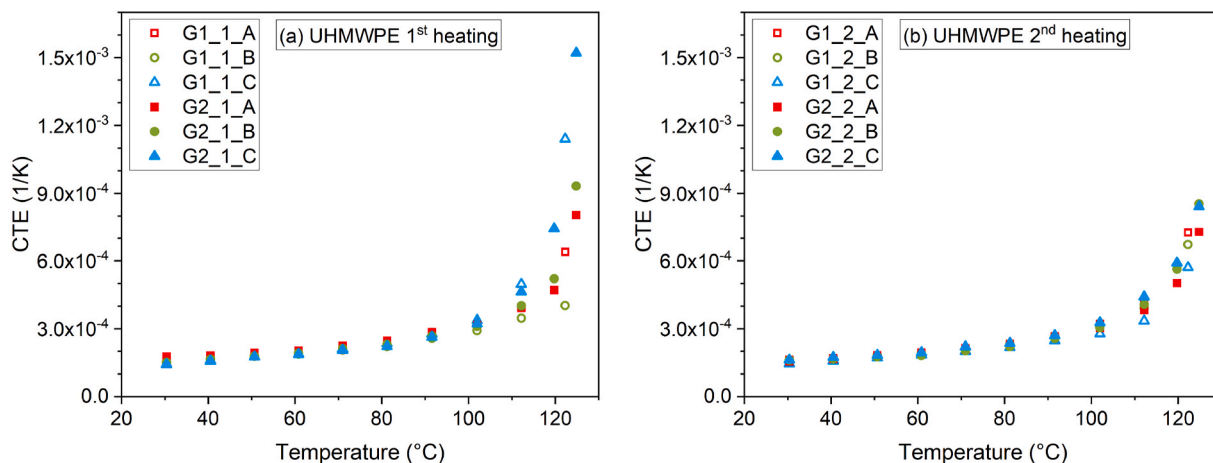


Fig. 8. Coefficient of thermal expansion (CTE) of two different UHMWPE samples during (a) first heating and (b) second heating in the three spatial directions A, B and C. Sample 1 is represented by open symbols, sample 2 by full symbols.

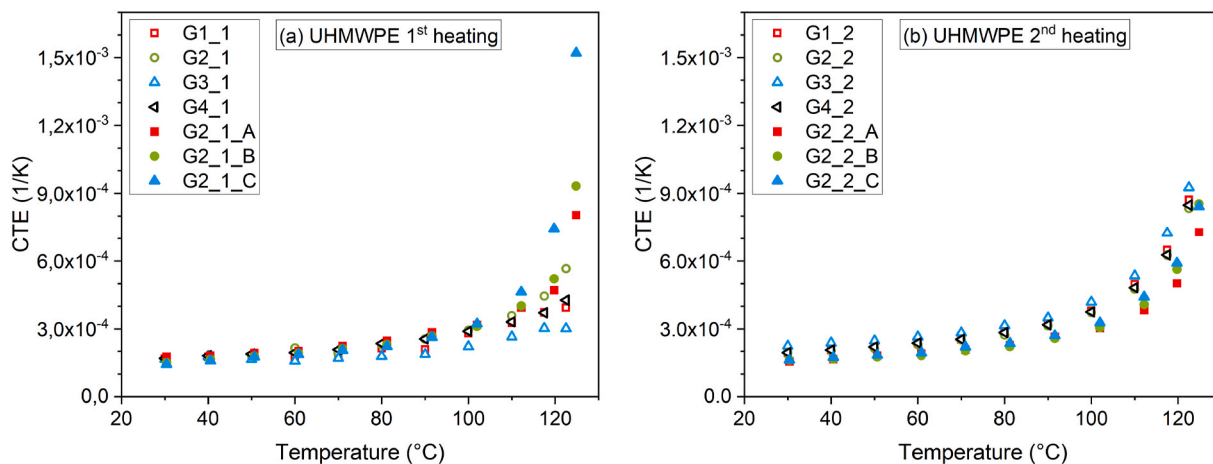


Fig. 9. Coefficient of thermal expansion (CTE) of UHMWPE samples measured using conventional TMA (open symbols) and in different directions using the new device (full symbols, sample G2) during (a) first heating and (b) second heating.

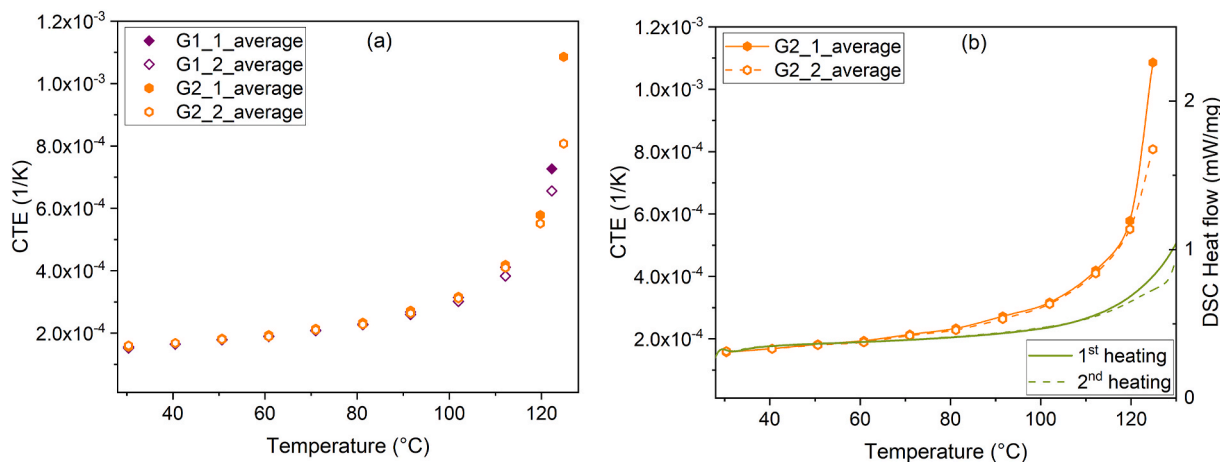


Fig. 10. Coefficient of thermal expansion (CTE), averaged over the three spatial directions for (a) two different UHMWPE samples and (b) UHMWPE sample G2 and DSC curves for untreated and annealed samples. The first heating/untreated sample is represented by a smooth line, the second heating/annealed sample by a broken line.

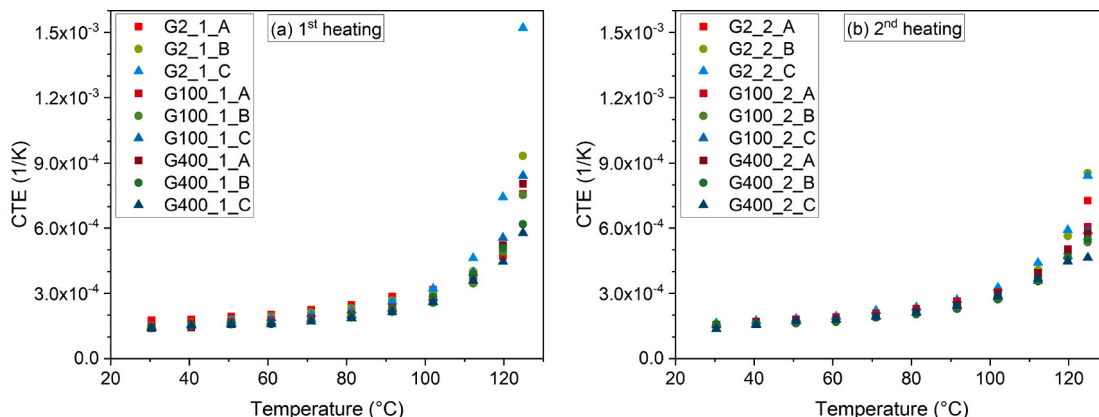


Fig. 11. Coefficient of thermal expansion (CTE) of neat and irradiated UHMWPE samples during (a) first heating and (b) second heating in the three spatial directions A, B and C.

anisotropic materials. Additionally, the time-consuming sample preparation can be avoided with the new test set-up. Furthermore, the new device can accommodate a larger range of samples dimensions, which also enables investigating the effect of sample size. On the other hand, it

is not suitable when only very small samples (mm-scale) are available. However, an influence of sample size on CTE as mentioned in literature was not clearly observed in the measurements, as the accordance with conventional small TMA samples was very good.

#### 4. Conclusions

A device was designed and built that allowed measuring the thermal expansion simultaneously in all three spatial directions on cubic samples with dimensions close to that of components in applications. The expansion was measured between 25 °C and 125 °C for two PE materials, one HMWPE and one tempered UHMWPE, for non-irradiated samples as well as cubes that have been irradiated with 100 and 400 kGy. The measured values lie mostly in the range of  $1\text{--}11 \times 10^{-4}$  1/K, showing good agreement with conventional TMA measurements on the same materials and with literature data for UHMWPE.

The HMWPE material shows a much stronger expansion in one direction compared to the other two directions during the first heating due to frozen stresses from processing. These stresses have mostly relaxed during the first heating, so that the expansion is more uniform in the second heating. By contrast, the tempered UHMWPE material shows only a slight difference between both heating runs, as the stresses from processing could already mostly relax during the tempering step by the manufacturer. The overall volumetric expansion is slightly lower at the highest temperatures in the second heating due to the annealing function of the first slow heating up to 125 °C, as supported by DSC measurements. The irradiation treatment does not affect the values significantly for the tested materials. The results enable a more realistic estimation of the thermal expansion behavior of the PE components under assembly conditions.

#### Author statement

Tobias Grelle participated in developing the method and conducted most of the experiments when he was at BAM. However, by the time this article was written, he was no longer employee at BAM and currently works at GRS.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### References

- [1] S.M. Kurtz, *The UHMWPE Handbook: Ultra-high Molecular Weight Polyethylene in Total Joint Replacement*, Elsevier Science, 2004.
- [2] P.R. Sreekanth, S. Kanagaraj, Influence of MWCNTs and gamma irradiation on thermal characteristics of medical grade UHMWPE, *Bull. Mater. Sci.* 37 (2) (2014) 347–356.
- [3] J. Shapiro, *Radiation Protection: A Guide for Scientists, Regulators, and Physicians*, Harvard University Press, 2002.
- [4] D. Wolff, et al., (U)HMWPE as Neutron Radiation Shielding Materials: Impact of Gamma Radiation on Structure and Properties, in *Effects of Radiation on Nuclear Materials: 25th Volume*, ASTM International, 2013.
- [5] A. Kömmling, et al., Effect of high-dose gamma irradiation on (U)HMWPE neutron shielding materials, *Radiat. Phys. Chem.* 142 (2018) 29–33, <https://doi.org/10.1016/j.radphyschem.2017.02.014>.
- [6] A. Kömmling, et al., Discoloration effects of high-dose  $\gamma$ -irradiation and long-term thermal aging of (U)HMW-PE, *Int. J. Polym. Sci.* (2017), <https://doi.org/10.1155/2017/1362491>.
- [7] M. Slouf, et al., Structural changes of UHMWPE after e-beam irradiation and thermal treatment, *J. Biomed. Mater. Res. B Appl. Biomater.* 85 (1) (2008) 240–251.
- [8] G. Gao, J. Fu, Highly crosslinked UHMWPE for joint implants, in: J. Fu, Z.-M. Jin, J.-W. Wang (Eds.), *UHMWPE Biomaterials for Joint Implants: Structures, Properties and Clinical Performance*, Springer Singapore, Singapore, 2019, pp. 21–68.
- [9] J.D.P. Menczel, R.B. Prime (Eds.), *Thermal Analysis of Polymers*, Wiley, New Jersey, 2009.
- [10] E.C. Willis, *Thermal Characterization of Commercial HDPE and UHMWPE*, Los Alamos National Lab.(LANL), Los Alamos, NM (United States), 2018.
- [11] D.J. Pastine, Volume dependence of the thermal expansion of polymers, *J. Appl. Phys.* 41 (13) (1970) 5085–5087.
- [12] G.K. White, C.L. Choy, Thermal expansion and Grüneisen parameters of isotropic and oriented polyethylene, *J. Polym. Sci. Polym. Phys. Ed* 22 (5) (1984) 835–846, <https://doi.org/10.1002/pol.1984.180220505>.
- [13] C.L. Choy, F.C. Chen, E.L. Ong, anisotropic thermal expansion of oriented crystalline polymers, *Polymer* 20 (10) (1979) 1191–1198, [https://doi.org/10.1016/0032-3861\(79\)90142-3](https://doi.org/10.1016/0032-3861(79)90142-3).
- [14] K. Miller, K. Ramani, Process-induced residual stresses in compression molded UHMWPE, *Polym. Eng. Sci.* 39 (1) (1999) 110–118.
- [15] H.S. Jayanna, S.V. Subramanyam, Thermal expansion of irradiated polyethylene from 10 to 340 K, *J. Polym. Sci. B Polym. Phys.* 31 (9) (1993) 1095–1098, <https://doi.org/10.1002/polb.1993.090310905>.
- [16] Gottfried W. Ehrenstein, Gabriela Riedel, Pia Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München, 2004.
- [17] C.L. Choy, F.C. Chen, K. Young, Negative thermal expansion in oriented crystalline polymers, *J. Polym. Sci. Polym. Phys. Ed* 19 (2) (1981) 335–352, <https://doi.org/10.1002/pol.1981.180190213>.
- [18] K.T. Gillen, R.L. Clough, Quantitative confirmation of diffusion-limited oxidation theories, *Abstr. Pap. Am. Chem. Soc.* 200 (1990) 382.