Neutron Radiation Shielding Material Polyethylene: Consequences of Gamma Irradiation – 15062

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ABSTRACT

High and ultra-high molecular weight polyethylenes are high performance materials, which are predestined for a wide range of applications due to characteristics like high density, low weight, good dimensional stability, high chemical resistance, and high hydrogen content. These polymers are used in two demanding areas: as implant material in medical technology (only ultra-high molecular weight polyethylenes) and as a component for neutron shielding purposes in casks for storage and transport of radioactive waste. In the medical field (joint replacements) as well as during neutron radiation shielding application, high and ultra-high molecular weight polyethylenes are exposed to gamma irradiation: in the first case requested as sterilization process and for surface-crosslinking and in the second case existing as a side effect of inserting the radioactive material in the cask.
Given that polyethylene as shielding material has to withstand any type of degradation affecting safety relevant aspects to be applicable for long-term radiation shielding purposes for instance over a period of 40 years, the durability of the material is of special interest. High molecular weight polyethylene (HMW-PE; LUPOLEN 5261Z; Lyondell Basell) and ultra-high molecular weight polyethylene (UHMW-PE; GUR 4120; Ticona) were subjected to gamma radiation and afterwards thermally treated. The gamma doses used are in the range of 50 to 600 kGy and irradiation takes place at RT using a Co-60 source. The planned thermal treatment will take place at a temperature of 125 °C for periods of minimum 30 days and maximum of five years. With the applied conventional analytical techniques it is possible to detect structural changes of both types of polyethylene induced by gamma irradiation and certainly of thermal treatment. Through gamma irradiation melting temperature, crystallinity, and density, respectively increased. Furthermore both polyethylenes get oxidized and cross-linked. With regard to the special application as neutron radiation shielding material in casks for storage and transport of radioactive materials, the impact of irradiation lead to changes of material properties. A consolidated view indicates that the detected changes of the irradiated (U)HMW-PE are not safety relevant for long-term neutron radiation shielding purposes over a period of 40 years in Germany.

INTRODUCTION

High molecular weight polyethylene (HMW-PE) and ultra-high molecular weight polyethylenes (UHMW-PE) are high performance materials, which are predestined for a wide range of applications due to characteristics like high chemical resistance, low wear, and high hydrogen content. In addition to the application of (U)HMW-PE as sports equipment (sliding surface of snowboards, skis) and in mechanical engineering (materials for spur gears and chain guides) these polymers are used in two other and even more demanding areas: as implant material in

medical technology (only UHMW-PE) and as a component for neutron shielding purposes in casks for storage and transport of radioactive waste. This suitability can be traced back to the fact that high and ultra-high molecular weight polyethylenes possess extreme high hydrogen content. In the medical field (joint replacements) as well as during neutron radiation shielding application, high and ultra-high molecular weight polyethylenes are exposed to gamma irradiation: in the first case requested as sterilization process and for surface-crosslinking and in the second case existing as a side effect of inserting the radioactive material in the cask. Especially concerning their use in the field of medical technology, different types of UHMW-PE have been intensively studied. It is generally accepted that two concurrent and competitive processes, based on initial chain scission and subsequent reactions of C-centered radicals and molecular fragments, occur in PE as a consequence of radiation: radical recombination accounts for crosslinking, together with some disproportionation, formation of low molecular weight fragments, and recrystallization [1]. Furthermore, formation of oxygenated structures in the presence of traces of oxygen is a competitive process to those mentioned above. Gamma irradiation induced chain scission preferentially takes place in the amorphous phase and noncrystalline surface of crystallites and results in shorter polymer chains, fewer entanglements, and consequently, increased molecular mobility [2]. The latter enables folding of polymer segments and thus, crystal growth and increased perfection in the crystal lamellae [1], [3].
With regard to the long-term application of (U)HMW-PE as implant or neutron shielding material, respectively, it is necessary to understand the influence of gamma irradiation on the material properties. For this purpose samples were investigated, which were gamma irradiated at Synergy Health Radeberg GmbH (GS) with doses from 50 kGy up to 600 kGy. Afterwards a comparison was made with untreated material. A comparison of the material irradiated at Forschungszentrum Jülich (FZJ) and Helmholtz Zentrum Berlin (HZB) with untreated samples was already discussed in [4], [5].

RESULTS AND DISCUSSIONS

Differential Scanning Calorimetry (DSC)

The untreated and irradiated samples of HMW- and UHMW-PE were characterized by DSC by determining the melting temperature T_m and melting enthalpy. An impact of gamma irradiation on these quantities and thus on the degree of crystallinity was found. The degree of crystallinity was determined via integration of the melting peak and relating it to the reference value of the melting enthalpy of 293 J/g [6]. Through irradiation the melting peak is shifted to higher values in the first DSC heating run. Recrystallization and remelting of the sample in a subsequent DSC cooling and heating run led to a shift towards lower values of T_m. This is shown in Figure 1 for the highest dose using the example of UHMW-PE.
The dependency of the melting temperature shift on gamma radiation dose is shown in Figure 2 for UHMW-PE. Likewise the degree of crystallinity shows the same dependency on irradiation (Figure 3). It increased after gamma irradiation and showed a decrease after subsequent recrystallization and remelting. An explanation for the increase of degree of crystallinity is that the radiation induced chain scission, followed by improved crystallization due to higher molecular mobility of the released new free chain ends, is the predominant effect. The decrease after melting and recrystallization could be explained by a sterical hindrance of crystallization through the existence of crosslinks.

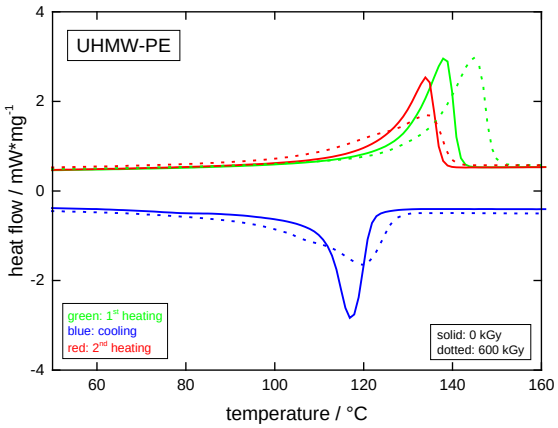

Fig. 1. Heating and cooling cycles of untreated and irradiated UHMW-PE samples

Oral et al. studied the degree of crystallinity of UHMW-PE in dependence on radiation dose and thermal treatment [7]. They also found an increase of degree of crystallinity through irradiation and a decrease after subsequent melting. Furthermore, T_m increased with increasing radiation dose and decreased with remelting. Stephens et al. analyzed the effect of dose rate on properties of UHMW-PE [8]. They observed an increase of melting temperature induced by irradiation, a crystallinity growth through irradiation and a decrease through subsequent melting. Furthermore they found a dependence of the determined parameter on the dose rate only for a high dose of irradiation.

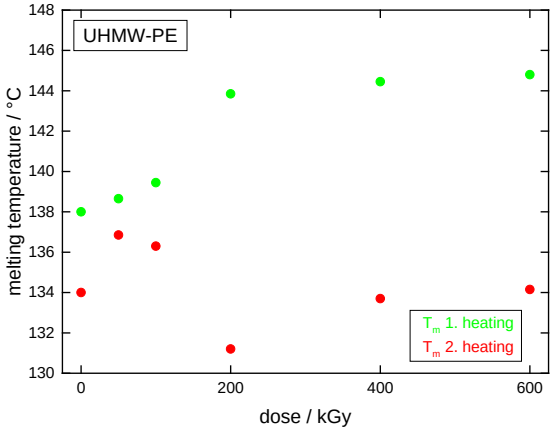

Fig. 2. Melting temperature in dependence of gamma irradiation dose for UHMW-PE

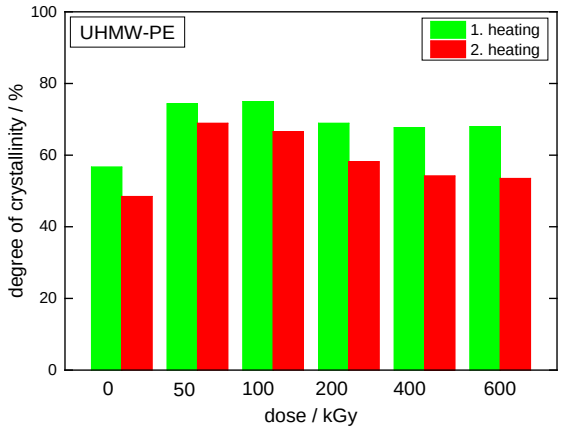

Fig. 3. Degree of crystallinity in dependence of gamma irradiation dose for UHMW-PE

Dynamic Mechanical Analysis (DMA)

DMA provides information about mechanical properties of a specimen as a function of time and temperature by subjecting it to a small, usually sinusoidal, oscillating force. Measured parameters are the storage modulus, the loss modulus, and the loss factor. The measurements were performed using a free oscillating torsional pendulum at 1 Hz.
The obtained curves of shear modulus G' for HMW-PE and UHMW-PE are shown in Figures 4 and 5. The principal temperature dependency of G' is similar for the untreated and the irradiated material and for HMW-PE as well as for UHMW-PE. With regard to the degree of crosslinking of the material, the plateau value of G' is of most interest.

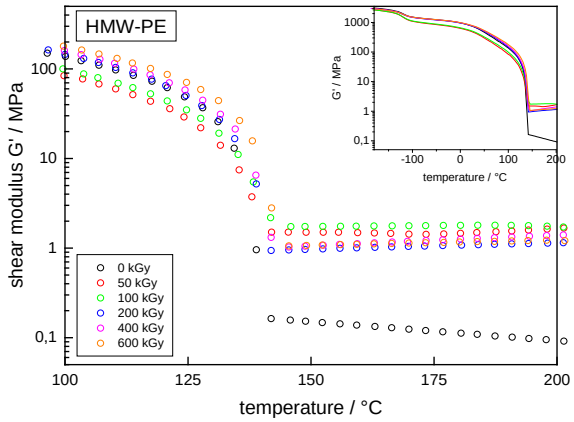

Fig. 4. Shear modulus G' of HMW-PE in dependence of gamma irradiation dose

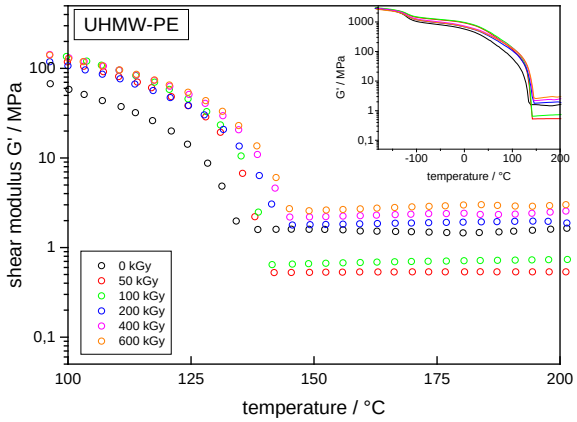

Fig. 5. Shear modulus G' of UHMW-PE in dependence of gamma irradiation dose

In comparison to all irradiated samples, the untreated HMW-PE shows lower plateau values for G'. Hence it can be concluded that irradiation led to more mechanically effective crosslinks of the material. However, it is not possible to identify if and how G' is dependent on the irradiation dose. Having a closer look at the slope of the plateau value with increasing temperature it can be clearly seen that the plateau values show a slight increase with increasing temperature in case of the irradiated samples. This provides an indication of chemical crosslinks, whereas the decrease of plateau values with increasing temperature for untreated sample could be understood as an indication for predominantly physical crosslinks (e.g. entanglements).
In case of UHMW-PE the relation of the plateau values is a similar one. Compared to the untreated sample the samples irradiated with a dose of 50 kGy respectively 100 kGy show lower plateau values of G'. It is assumed that low irradiation doses lead preferentially to chain scission and consequently to a smaller number of mechanically effective crosslinks. This results in a lower plateau value of G'. From an irradiation dose of 200 kGy on and higher, the G' plateau value is higher compared to the untreated material. This is an indication for more mechanically effective crosslinks due to irradiation. In addition the value increased with temperature which is an indication for chemical crosslinks.

FT-IR Spectroscopy

Another possibility to determine the existence of crosslinks and insertion of oxygen in the structure of polyethylene is the use of FT-IR spectroscopy. IR spectra of all samples were measured in transmission mode on samples with a thickness of 100 µm.
For the determination of structural differences induced by irradiation, special attention is paid to the absorption bands at 965 and 1700 cm^{-1}. The former band shows the absorbance of C=C bonds (trans-vinylene, −CH=CH−) and might be correlated to crosslinking. The latter represents the absorbance of C=O bonds in aldehydes, ketones and carboxyls and is a sign for the oxidation of the sample. The absorption at 2022 cm^{-1} was used as reference absorption peak corresponding to methyl group stretching [9].

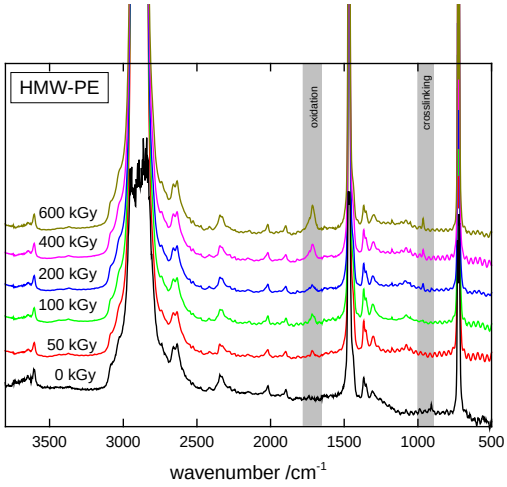

Fig. 6. FT-IR spectra of HMW-PE in dependence of the irradiation dose

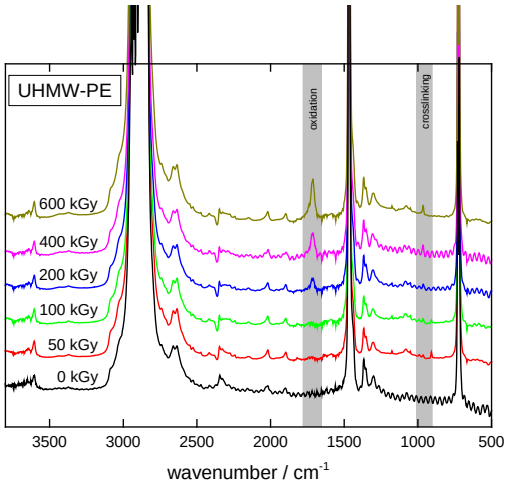

Fig. 7. FT-IR spectra of UHMW-PE in dependence of the irradiation dose

The obtained spectra of the analyzed untreated and irradiated samples of HMW- and UHMW-PE are shown in Figures 6 and 7. In principle all spectra of HMW-PE and also of UHMW-PE show close similarity independent of irradiation dose. The obtained spectra of the untreated (U)HMW-PE samples show neither an absorption band in the region of 965 cm^{-1} nor in the region of 1700 cm^{-1}. For HMW-PE an irradiation dose of 50 kGy leads to formation of an absorption band at 1700 cm^{-1} which intensity increases with increasing irradiation dose. An absorption band appears at a wavenumber of 965 cm^{-1} for an irradiation dose of 200 kGy and higher. The intensity of this band increases with further dose increase to values of 400 and 600 kGy. Based on the existence of the absorption band at 965 cm^{-1} it is assumed that hydrogen release and crosslinking of the sample take place for irradiation doses of 200 kGy and higher. The existence of the absorption band at 1700 cm^{-1} is an indication of sample oxidation. This oxidation is detectable for an irradiation dose of 50 kGy and higher. The obtained spectra of UHMW-PE show a similar behavior. An irradiation of 200 kGy leads to a formation of an absorption band at

1700 cm^{-1} as well as an absorption band at 965 cm^{-1}. Both absorption bands get more intense with increasing irradiation dose. Consequently it is possible to detect crosslinking – and hydrogen release – as well as oxidation of the sample with FT-IR for irradiation doses of 200 kGy and higher.
There are several publications, e.g. Slouf et al. [10], describing the same changes in FT-IR spectra after irradiation (gamma, e-beam) of polymers. In most cases, the changes in the absorption bands were determined in dependence of the irradiation dose, and it was found that increasing the dose induced a higher intensity of the absorption bands of carbonyl and trans-vinylene groups.

Degree of Crosslinking

In addition, the degree of crosslinking of the irradiated samples in comparison with the untreated ones was determined according to DIN 16892 [11], where the amount of insoluble sample content is assigned as degree of crosslinking. For the definition of the insoluble content, the sample was extracted by exposure to refluxing boiling xylene. The weight was determined before and after this treatment. As a result, an increase of crosslinks with increasing the gamma irradiation dose was determined for both HMW-PE (Figure 8) and UHMW-PE (Figure 9). In case of UHMW-PE the insoluble content of about 30 % for the untreated material is due to the entanglements of the extreme long polymer chains. These findings support the results of the FT-IR spectroscopy.
Oral et al. supported our findings with their results, although they used a different method [12]. Elzubair et al. analyzed the correlation between irradiation and its influence on the gel fraction [13]. They also found that increasing the irradiation dose led to an increase of the gel fraction and a decrease of the swelling ratio.

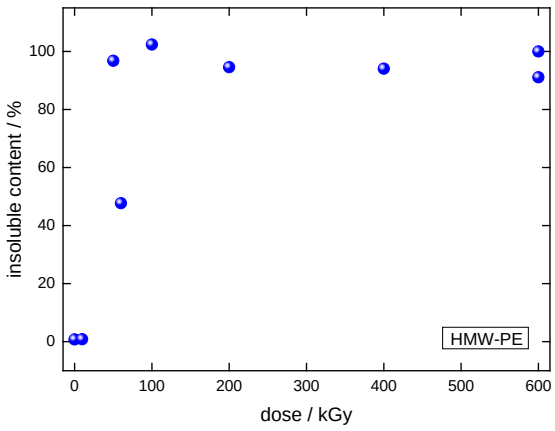

Fig. 8. Insoluble content of HMW-PE in dependence of irradiation dose

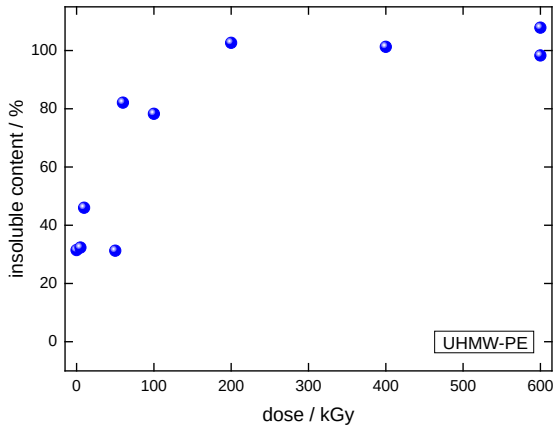

Fig. 9. Insoluble content of UHMW-PE in dependence of irradiation dose

Density Measurements

The density of all samples was determined via immersion method. An analytical balance was used with an accuracy of 0.1 mg. Water was used as immersion liquid. The samples were weighed at air and under water and the measurements were performed at a temperature of 23 °C and a relative humidity of 50 %. Figure 10 summarizes the obtained density values of the samples which were gamma-irradiated without any further treatment.

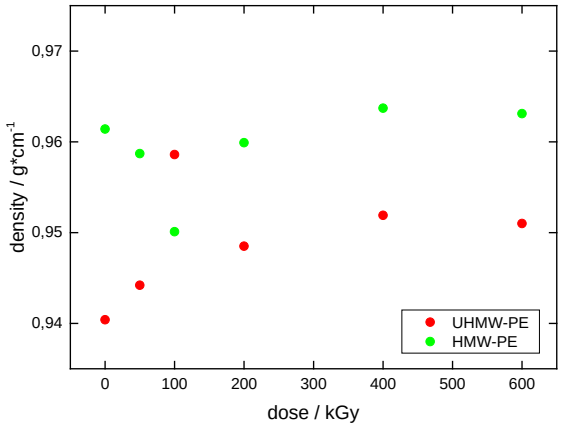

Fig. 10. Density values of HMW-PE and UHMW-PE in dependence of gamma irradiation dose

The density of HMW-PE as well as of UHMW-PE increases with an increasing dose of gamma irradiation. This is a positive aspect due to the fact that the density is an important criterion for the shielding properties of polyethylene.

CONCLUSION

With the applied methods it is possible to detect structural changes of (U)HMW-PE induced by gamma irradiation. The gamma irradiation led to an increase of the degree of crystallinity and of the plateau value of shear modulus G'. Additionally the irradiation induced an oxidation and crosslinking of the samples and an increase of the insoluble content.
With regard to the special application of (U)HMW-PE as neutron shielding material in casks for storage and transport of radioactive material it is possible to make the statement that the detected changes of the irradiated (U)HMW-PE are not safety relevant for long-term neutron radiation shielding purposes over a period of 40 years in Germany.

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