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RADIATION INDUCED STRUCTURAL CHANGES OF (U)HMW POLYETHYLENE WITH REGARD TO ITS APPLICATION FOR RADIATION SHIELDING

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ABSTRACT

The special properties of high molecular weight polyethylene (HMW-PE) and ultra high molecular weight polyethylene (UHMW-PE) result basically from their extreme chain lengths and their high degree of crystallinity. As high-performance polymers, they are used for a variety of applications. UHMW-PE in particular is often utilized for endoprothesis (due to its excellent slip and wear properties) and due to its high hydrogen content as a neutron moderator in casks for storage and transport of radioactive materials.

To prepare the material for instance for its use as a total joint replacement, it is exposed to radiation for several reasons, such as sterilization and crosslinking, leading to partial improvement of the mechanical properties (e.g. fracture toughness, crack propagation resistance, wear resistance) and better chemical stability.

To be applicable for long term radiation shielding purposes for instance over a period of 40 years, PE has to withstand any type of degradation affecting safety relevant aspects.

The scope of our investigation comprises an estimation of the radiation impact on the molecular and supra molecular structure of two types of PE and to what extent these changes are detectable by thermo-analytical (TA) methods, such as Differential Scanning Calorimetry (DSC), Thermo Mechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA) and Thermo Gravimetric Analysis (TGA). Additionally FT-IR spectroscopy as well as density and gas sorption measurements were carried out.

Due to the poor solubility of HMW-PE and UHMW-PE, some classical analytical techniques are not applicable. But TA-methods represent a feasible approach to detect structural and morphological features of these materials as well as changes caused by external influences, such as thermal treatment and/or irradiation. With the combination of the applied TA-techniques it is possible to distinguish between crosslinking and degradation.

INTRODUCTION

UHMW-PE has been used for several years in medical technology due to its excellent slip and wear properties. Besides this, (U)HMW-PE − due to their high hydrogen content − are used as neutron shielding material in casks for storage and transport of radioactive materials.

In both cases, irradiation and its impact on the molecular structure of polyethylene play an important role. In the first case, irradiation is applied deliberately for purposes such as sterilization and crosslinking, leading to partial improvement of the mechanical properties (e.g. fracture toughness, crack propagation resistance, wear resistance) and better chemical stability [1,2,3]. In the second case irradiation exists as a by-product of inserting the radioactive material in the cask. Hence PE 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.

Specifically concerning their use in the field of medical technology, (U)HMW-PE have been objects of numerous publications. It is generally accepted that two parallel and competitive processes, based on chain scission and 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 [4]. Furthermore, formation of oxygenated structures in the presence of traces of oxygen is an antagonist of the C-centered radicals. Radiation induced scission preferentially takes place in the amorphous phase and noncrystalline surface of the crystals. It is followed by folding of molecular fragments, crystallinity growth and increased perfection in the crystal lamellae [4,5]. Chain scission results in shorter polymer molecules, fewer entanglements, and consequently, increased molecular mobility [6].

The scope of our investigation comprises an estimation of the radiation and thermal impact on the molecular and supra molecular structure of the two types of PE used for neutron shielding cask components. A further point which is worth to explore is to what extent these changes are detectable by thermo-analytical (TA) methods, such as Differential Scanning Calorimetry (DSC), Thermo Mechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA) and Thermo Gravimetric Analysis (TGA). Additionally density and FT-IR measurements have been performed.

In our studies we focused on two materials: HMW-PE (LUPOLEN 5261Z) and UHMW-PE (GUR 4120). Both materials were γ-irradiated (dose of ~600 kGy) at RT under inert conditions. For HMW-PE one set and for UHMW-PE two sets of irradiated samples were investigated. In the following the obtained results will be presented and discussed.

RESULTS AND DISCUSSION

Determination of T_m, and degree of crystallinity by DSC

The untreated and irradiated samples of high and ultra high molecular weight polyethylene were characterized by Differential Scanning Calorimetry by determining the melting temperature, the melting enthalpy, and the degree of crystallinity.

The weight of the DSC samples was in average 10 mg and they were placed in aluminium sample pans. The sample and the reference were heated with a heating rate of 10 K/min from -100 to 160 °C, cooled to -100 °C. A total of three heating and two cooling cycles were performed for each measurement. The melting temperature was determined as the maximum of the enthalpy peak, the degree of crystallinity was determined via integration of the enthalpy peak and normalizing it with the reference value of the enthalpy of melting of 100 % crystalline polyethylene, 293 J/g [7]. During our studies we found an impact of γ-irradiation on melting temperature, melting enthalpie, and degree of crystallinity. Figure 1 shows the heating cycles of HMW-PE. Through irradiation the melting peak and so the melting temperature is shifted to higher values. Subsequent recrystallization and remelting led to a shift towards lower values of melting temperature. All measured melting temperatures for (U)HMW-PE are summed up in Figure 2.

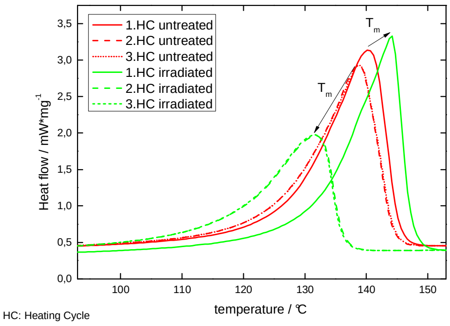

Figure 1: Heating cycles of untreated HMW-PE compared to irradiated HMW-PE

Likewise the degree of crystallinity (Figure 3) shows the same dependency on irradiation. Through irradiation it increased and showed a decrease after subsequent recrystallization and remelting. A suggested reason for the increase of crystallinity is that the radiation induced chain scission, followed by increased crystallization due to higher molecular mobility of the released new free chain segments, is the predominant effect. The decrease after melting and recrystallization could be explained by a sterical hindrance of the crystallization through the existence of crosslinks.

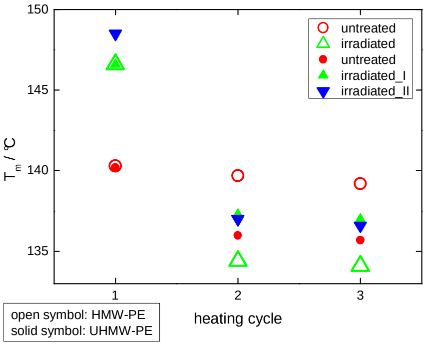

Figure 2: Melting temperatures of (U)HMW-PE

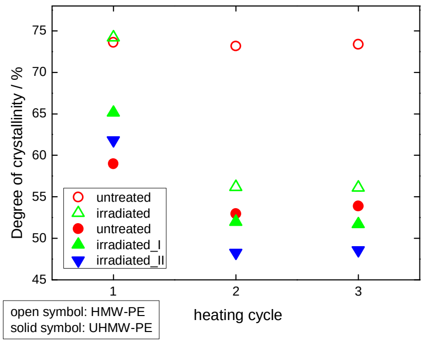

Figure 3: Degree of crystallinity of (U)HMW-PE

Oral and coworkers (2008) studied the degree of crystallinity in dependence on irradiation dose and thermal treatment [8]. They also found an increase of crystallinity through irradiation and a decrease after subsequent melting. Furthermore, they took a close look on T_m. It increased with increasing radiation dose and decreased with remelting. Stephens et al. (2005) analyzed the effect of dose rate on the properties of UHMW-PE [9]. They found an increase of melting temperature induced by irradiation, a crystallinity growth through irradiation and a decrease through subsequent melting.

Determination of the thermal expansion coefficient via Thermo Mechanical Analysis

Especially with regard to the position of the neutron moderator rods in the wall of the cask, one important aspect is the expansion due to thermal impact induced by the inserted radioactive material. For an analytical determination of the thermal expansion behavior over the entire considered temperature range, thermo mechanical measurements of the untreated samples were performed and compared to those of the irradiated ones.

The samples had an edge length of 6 mm and the measurements were performed under nitrogen atmosphere. The samples were heated from -70 °C up to 200 °C with a heating rate of 10 K/min, afterwards cooled down to -70 °C (rate of 2 K/min), during the second heating cycle the sample was heated up to 220 °C. The linear expansion coefficient was graphically determined by applying a tangent to the slope of the measured curve. The obtained values of the linear expansion coefficient were summed up in the following Table 1.

Table 1: Thermal expansion coefficients of HMW-PE und UHMW-PE

sample	treatment	α (T<60°C) [K^{-1}*10^{-4}]	α (T>160°C) [K^{-1}*10^{-4}]
HMW-PE	untreated	0,643 (1.HC)	-
HMW-PE	*irradiated*	*1,43*	*2,85*
UHMW-PE	untreated	2,47	3,12
UHMW-PE_I	*irradiated*	*1,42*	*2,62*
UHMW-PE_II	*irradiated*	*1,46*	*2,94*

Even though the values of the expansion coefficient were determined from the second heating cycle (known thermal history of the sample) it made sense to have a closer look at the first heating cycle. Especially here the untreated HMW-PE showed a quite different behavior. It started to flow, so running a second heating cycle was impossible, whereas due to crosslinking the irradiated HMW-PE sample did not start to flow to that extent. The expansion coefficients of irradiated HMW-PE and UHMW-PE were similar. Untreated UHMW-PE clearly showed larger thermal expansion coefficients compared to all other tested materials.

Thermal degradation behavior by means of Thermogravimetry

The behavior of the polyethylene in the case of fire constitutes an important safety aspect. For this purpose of understanding the behavior thermo-gravimetric measurements were performed. In general there are two possibilities to determine the degradation behavior: under inert atmosphere (pyrolysis) and under oxygen atmosphere (thermo-oxidative degradation).

The thermal degradation behavior of our samples was analyzed under both atmospheres, under inert gas (pyrolysis) and under synthetic air (thermo-oxidative degradation). The samples had in average a weight of 10 mg. Under inert gas atmosphere the sample was heated from 25 °C up to 600 °C in a nitrogen atmosphere, under synthetic air the sample was heated from 25 °C up to 600 °C. For both methods the heating rate was 10 K/min. The type of degradation (single-step, two-step process) and the corresponding peak temperature were determined graphically.

Even though degradation under inert atmosphere best reflects the realistic circumstances (moderator is installed in separated bore holes with residual oxygen only), the obtained curves were compared to that measured under oxygen (for HMW-PE see Figure 4). In an inert atmosphere, HMW-PE as well as UHMW-PE showed a single-step degradation, which started at slightly lower temperatures (difference 5 °C) for the irradiated samples. At a temperature range from 440 to 490 °C a massive weight loss of the samples can be observed. After completion the sample has a weight of almost zero. Compared to that, the measurements under oxygen atmosphere showed that an insertion of oxygen (increase of weight at temperature range of 240 to 250 °C) took place first, afterwards the degradation started. This time a two-step process was observed: first the oxygenated structures degraded and one fourth of the original mass was lost. However the main loss of weight could be observed at the second step of degradation at slightly lower peak temperatures as for the inert atmosphere. Slouf et al. (2008) had performed thermo gravimetric measurements, too [14]. They also measured in air and observed a mass increase due to absorption of oxygen.

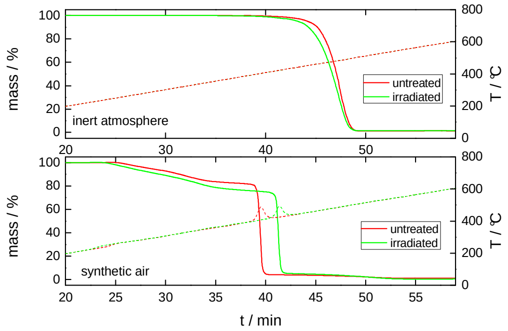

Figure 4: Thermo gravimetric measurements of HMW-PE under inert and oxygen atmosphere

Dynamic Mechanical Analysis DMA

Dynamic mechanical analysis (DMA) provides information about the 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 complex modulus, the storage modulus, the loss modulus, and the loss factor.

The presented measurements were performed at a frequency of 10 Hz. The heating rate was 1 K/min in a temperature range from -180 °C up to 200 °C.

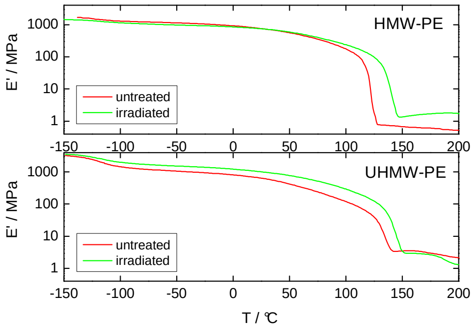

Figure 5: DMA curves of HMW-PE and UHMW-PE

In Figure 5 the obtained curves of storage modulus for untreated and irradiated samples for HMW-PE as well as for UHMW-PE are given. They show large similarities except for the strong decrease in the temperature range between 120 °C and 150 °C. This strong decrease – two orders of magnitude – of storage modulus is shifted to higher temperatures for the irradiated samples. This shift supports the obtained results from DSC measurements.

The plateau value of the storage modulus is an indication for the degree of crosslinking of a polymer. In case of HMW-PE, the irradiated sample shows a higher plateau value so it might be concluded that the degree of crosslinking is increased through irradiation. This would support the results from solubility measurements.

In contrary to this, UHMW-PE, apparently not influenced by irradiation, show similar plateau values. But because of the longer polymer chains for UHMW-PE also a higher amount of physical crosslinking (for instance entanglements) has to be taken into account.

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. Infrared spectroscopy spectra of all samples were measured in transmission mode.

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 the methyl group stretching [13].

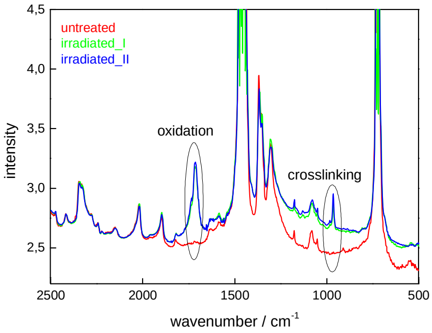

Figure 6: FT-IR spectra of untreated and irradiated UHMW-PE

Exemplarily, the obtained spectra of the untreated and irradiated UHMW-PE are presented in Figure 6. They show large similarities, except for the formation of two new absorption bands at 965 and 1700 cm^{-1} in the spectra of both irradiated materials. Both absorption bands are a sign for the modification of the molecular structure of the polyethylene induced by γ-irradiation.

There are several publications, including Slouf et al. (2008) and Tretinnikov et al. (1999), describing the same changes in FT-IR spectra after irradiation (γ, e-beam) of polymers [14,15]. In most cases, the changes in the absorption bands were determined in dependence on 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.

Density measurements

The density of all samples (untreated, irradiated, irradiated and remelted) was determined with a density gradient column. The samples arranged according to their density along the gradient of the column. By means of their position in cm and a calibration curve the density was calculated. As solvent a mixture of diethylene glycol and isopropanol (ratio 1:1.3) was used, the gradient was 0.86 – 1.00 g/cm^{-1} with a tolerance of 0.001 g/cm^{-1}.

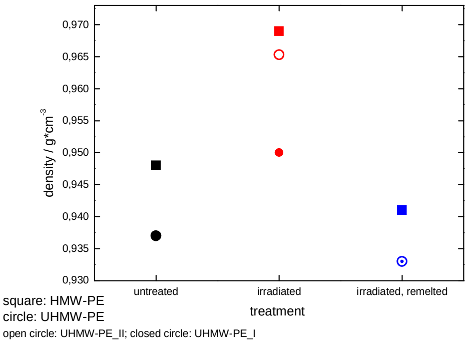

Figure 7: Density values of (U)HMW-PE

Figure 7 summarizes the determined values of density of the described materials. Density measurements of all samples support the results obtained by DSC. The density increased as a result of irradiation and therefore so did the degree of crystallinity, and after remelting and subsequent recrystallization the density − and thus the degree of crystallinity − shows a decrease.

Degree of crosslinking

In addition, the degree of crosslinking of the irradiated samples in comparison with the untreated ones was determined (DIN 16892), where the amount of insoluble sample content is assigned as degree of crosslinking [10]. For the definition of the insoluble part, the sample was extracted by exposure to refluxing boiling xylene. The weight was determined before and after this treatment.
The result of this was a huge increase of crosslinking induced by γ-irradiation (Figure 8).

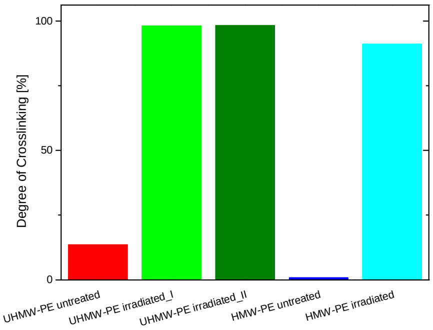

Figure 8: Degree of crosslinking of untreated and irradiated (U)HMW-PE

Oral et al. (2008) supported our findings with their results, although they used a different method [11]. Elzubair et al. (2003) analyzed the correlation between irradiation and its influence on the gel fraction [12]. They also found that increasing the irradiation dose led to an increase of the gel fraction and a decrease of the swelling ratio.

CONCLUSIONS

With the applied methods it is possible to detect structural changes of polyethylene induced by γ-irradiation. The detected changes of the irradiated material are not safety relevant for the application of polyethylene as moderator material; contrarily, some properties actually improve via irradiation.
However, so far we have only made a comparison between untreated and high dose irradiated material. In the future we plan to analyze samples irradiated with different doses and different dose rates.

ACKNOWLEDGMENTS

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