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The Effect of Electron Beam Radiation on the Molecular Structure of Ultra-high Molar Mass Polyethylene Used for Medical Implants

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Summary: Systematic investigations on the influence of electron beam radiation of different dosage on molecular degradation as well as crosslinking of ultra-high molar mass polyethylene containing various amounts of α-tocopherol as stabilizer were carried out in air and an inert nitrogen atmosphere. The samples were analyzed with respect to their content of insoluble crosslinked fraction and the molar mass distribution of the soluble fraction. The extent of crosslinking and degradation is dependend on the absorbed dosage of the radiation. The crosslinking process is favored in nitrogen atmosphere whereas in air molecular degradation is increasing. The extent of crosslinking as well as degradation can be reduced by the addition of α-tocopherol both, in air and nitrogen.

Introduction

Polyethylene of ultra-high molar mass (UHMW-PE) is being used for medical implants since the 1960s.[1] The in-vivo oxidation leads to a molecular degradation of the UHMW-PE and therefore to a higher brittleness of the material which may cause permanent inflammation of the tissue.[2-5] A possible way to overcome this problem is the addition of α-tocopherol, a biocompatible stabilizer, to the UHMW-PE prior to sintering to avoid degradation.[6,7] In addition, the properties of the UHMW-PE implants may be further improved by crosslinking of the material. This usually occures during the sterilization process as a consequence of the γ- or electron beam irradiation in vacuum or an inert atmosphere.

High-energy irradiation generally causes two antagonistic processes, crosslinking and random scission of the polymer chain, of which one usually predominates over the other.[8]

Starting from the pure UHMW-PE powder containing different amounts of α-tocopherol, sintered specimens were produced with subsequent electron beam irradiation in the same way as for medical implants. Different dosages of radiation in air and nitrogen were applied to

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study the influence on the degree of crosslinking and molar mass distribution of the soluble fraction.

Experimental

Sample preparation

The UHMW-PE powder "GUR 1020" (Ticona GmbH, former Hoechst AG, Frankfurt/Main, Germany) was homogeneously mixed with α-tocopherol (Hoffmann-LaRoche AG, Basel, Switzerland) and sintered for 7 hours (230 °C, 35 bar) at Isosport GmbH, Eisenstadt, Austria. The electron beam irradiation (absorbed dosage: 10 to 100 kGy) was carried out at Mediscan GmbH, Kremsmünster, Austria with the 10 MeV linear accelerator TB-10/15 from Titan Beta, Dublin, CA, USA.

Determination of the insoluble fraction

Specimens of a diameter of 10mm and a thickness of 300 μm were placed in 50 mL of 1,2,4-trichloro benzene (TCB) containing 0.0125 % 2,6-di-tert.-butyl-(4-methylphenol) (BHT) for 3 hours at 145 °C in nitrogen atmosphere. The specimens were then dried for 24 hours at 80 °C in vacuum and the remaining insoluble crosslinked polymer determined gravimetrically. The ratio of molecular degradation and crosslinking G(S)/G(X) was calculated according to Charlesby and Pinner[9] (see Equation 1).

$$s + s^{0.5} = G(S) / 2G(X) + 100 \cdot N_A / M_{w,0} \cdot G(X) \cdot D \qquad (1)$$

with s: soluble fraction, G(S): number of broken main chain bonds per 100 eV, G(X): number of newly formed intermolecular linkages per 100 eV, N_A: Avogadro's constant ($6.023 \cdot 10^{23}$ mol^{-1}), $M_{w,0}$: weight average molar mass of the initial sample, and D: absorbed dosage in eV/g.

Size exclusion chromatography (SEC)

The molar mass distribution was determined at 135 °C with the "GPC 220" chromatograph (Polymer Laboratories, Church Stretton, UK) coupled with the low-angle laser light scattering detector KMX 6 (Chromatix, Sunnyvale, CA, USA). A set of two columns of PLgel Mixed-ALS of Polymer Laboratories (gel particle size: 20 μm, "low bleeding" columns for light scattering detectors) was used. TCB containing 0.0125 % BHT served as solvent. The flow rate was set to 0.2 mL/min to avoid molecular degradation during the SEC run.[10,11]

Results and discussion

As can be seen from Table 1, the pure UHMW-PE powder is completely soluble with a weight average molar mass, M_w, of 5,700 kg/mol and contains molar mass fractions up to 50,000 kg/mol (see Figure 1).

Table 1. Mass content of the insoluble gel fraction, weight average molar mass M_w and polydisperisty parameter PD ($PD = M_w/M_n$, M_n: number average molar mass) of the soluble fraction of the UHMW-PE prior to and after sintering with different mass contents of α-tocopherol as stabilizer.

mass content of α-tocopherol / %	insoluble gel fraction / %	M_w / $kg \cdot mol^{-1}$	PD
$0^{a)}$	0	5,700	2.9
$0^{b)}$	48	2,900	2.3
$0.2^{b)}$	28	3,600	2.1
$0.4^{b)}$	26	3,600	2.2
$0.8^{b)}$	20	3,800	2.2

$^{a)}$ Pure UHMW-PE powder, not sintered.

$^{b)}$ Sintered samples.

After the sintering process the mass content of insoluble gel is about 50 % and the molar mass of the soluble fraction decreases to a weight average value of 2,900 kg/mol. This value corresponds to $M_{w,0}$ in Equation 1. The highest molar mass fraction only reaches a value of $M_w \approx 20{,}000$ kg/mol (cf. Figure 1). As also can be seen from Figure 1, the molar mass distribution curves of the pure UHMW-PE powder as well as the unstabilized, sintered UHMW-PE sample start approximately at the same molar mass of 120 kg/mol, indicating that no molecular degradation occurred during the sintering process. The soluble fraction of the sintered sample contains less molecules of ultra-high molar mass than the pure UHMW-PE powder. This suggests that the molecules of high molar mass are preferably crosslinked during the sintering process.

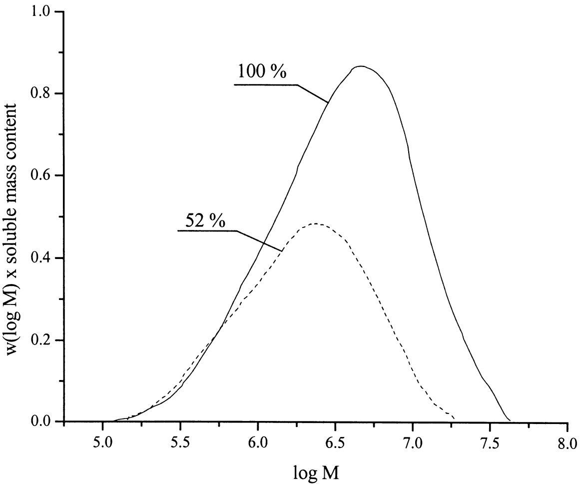

Figure 1. Molar mass distribution of the pure UHMW-PE powder (solid line) and the soluble fraction of the unstabilized, sintered UHMW-PE (dashed line). The areas of the distribution curves correlate to the mass content in percentage of the soluble fraction of the samples.

The addition of stabilizer to the UHMW-PE prior to sintering reduces the content of the insoluble fraction from 48 % to 20 % in the case of 0.8 % α-tocopherol where the value of M_w of the soluble fraction increases to 3,800 kg/mol. The polydispersity factor PD ($PD=M_w/M_n$, M_n: number average molar mass) of each of the sintered samples is close to 2, suggesting that the soluble fractions have mainly undergone a random scission process.

Samples irradiated with different dosage of electron beam clearly show a dependency of molecular degradation and crosslinking on the absorbed dose. Figure 2 shows the Charlesby-Pinner plot (cf. Equation 1) of the term $s+s^{0.5}$, representing the content of soluble fraction, as a function of the inverse dosage D^{-1} for the stabilized and unstabilized samples irradiated in air and nitrogen atmosphere.

As can be seen from Figure 2 the soluble fraction of the polymer never disappears completely. At an infinite dose it reaches the value of G(S)/2G(X) (cf. Equation 1) representing the ratio of molecular degradation and crosslinking.

The same sample irradiated in air shows higher values of $s+s^{0.5}$ indicating a change in the ratio of G(S)/2G(X). This means that the molecular degradation is now favored compared to crosslinking. In the case of the stabilized samples the slopes of these curves are approximately twice as large as for the unstabilized samples. The stabilizer acts as a scavenger for free radicals and the crosslinking process is hindered.

The values of $s+s^{0.5}$ at infinite dosage as well as G(S)/G(X) are summarized in Table 2.

The highest possible content of insoluble gel fraction at infinite dosage, the limiting gel fraction, can be obtained from the intercept of the $s+s^{0.5}$ axis (cf. Figure 2). The addition of α-tocopherol as well as an irradiation in air reduces the limiting gel fraction.

The ratio of G(S)/G(X) never exceeds the value of 0.88. Since for all values of G(S)/G(X)<4 crosslinking predominates over the molecular degradation,[9] under the applied conditions there is no danger of a complete degradation of the UHMW-PE.

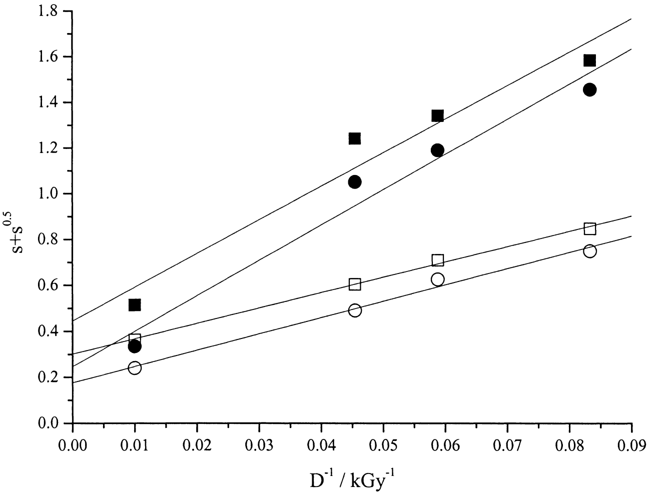

Figure 2. Plot of $s+s^{0.5}$ as a function of D^{-1} according to Charlesby and Pinner (see text). Stabilized (0.8 % α-tocopherol; closed symbols) and unstabilized (open symbols) sintered UHMW-PE samples, irradiated in nitrogen atmosphere (○, ●) and in air (□, ■) with electron beam of varying dosage.

Typical molar mass distribution curves of the soluble fraction of the samples stabilized with 0.8 % of α-tocopherol after electron beam irradiation (absorbed dose: 10, 22, and 100 kGy) in nitrogen are depicted in Figure 3.

Table 2. Values of $s+s^{0.5}$ and G(S)/G(X) according to Charlesby and Pinner as well as the limiting gel fraction (see text) for the unstabilized and stabilized (content of α-tocopherol: 0.8 %) sintered UHMW-PE samples irradiated in air and nitrogen atmosphere with electron beam.

UHMW-PE sample / irradiation atmosphere	$s+s^{0.5}$ at $D^{-1} = 0$	G(S)/G(X)	limiting gel fraction / %
unstabilized / nitrogen	0.17	0.34	98
unstabilized / air	0.30	0.60	94
stabilized / nitrogen	0.25	0.50	96
stabilized / air	0.44	0.88	89

An increasing absorbed dosage leads to a shift of the molar mass distribution curves towards lower molar masses. Due to molecular degradation the low molar mass tail is shifted from 45 kg/mol in the case of 10 kGy absorbed dosage to 38 kg/mol at 22 kGy to finally 18 kg/mol in the case of 100 kGy. The areas of the molar mass distribution curves in Figure 3 correlate to the soluble mass content of the samples.

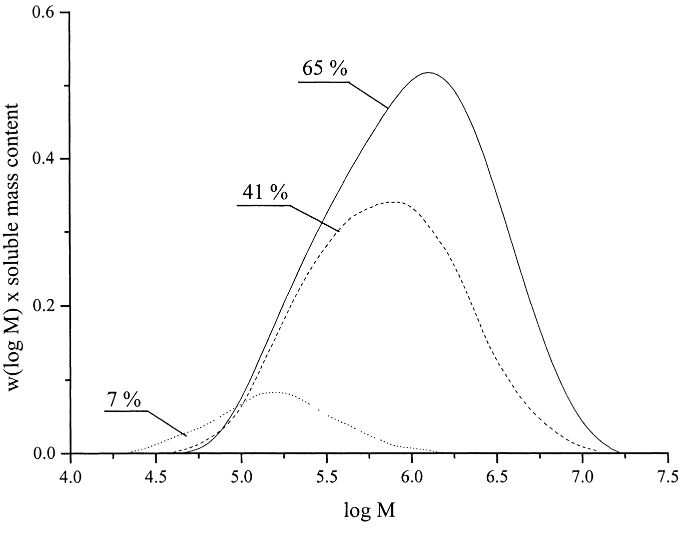

Figure 3. Molar mass distribution curves of the soluble fraction of the sintered UHMW-PE samples containing 0.8 % of α-tocopherol after electron beam irradiation in nitrogen atmosphere with 10 (solid line), 22 (dashed line), and 100 kGy (dotted line). The areas of the distribution curves correlate to the mass content in percentage of soluble fraction of the samples.

The molecular degradation can also be observed by the decrease of the weight average molar masses, M_w, as they are collected in Table 3. The values of M_w of the unstabilized samples do not vary significantly with the atmosphere in which the irradiation was carried out or the absorbed dosage, except the sample with an absorbed dosage of 100 kGy. As could already be seen in Figure 2, irradiation in nitrogen favores the crosslinking process.

In the case of the soluble fraction of the samples stabilized with 0.8 % of α-tocopherol it can be seen from Table 3 that the stabilizer loses a lot of its efficiency when the irradiation is carried out in air. The samples irradiated in an inert nitrogen atmosphere possess higher values of M_w, however, they are less soluble (cf. Figure 2 and Table 2). α-Tocopherol, which acts as a scavenger for free radicals is used up by the oxygen in the air and therefore, molecr degradation as well as crosslinking is no longer hindered.

Table 3. Weight average molar masses, M_w, of the soluble fraction of the sintered, stabilized (0.8 % α-tocopherol) and unstabilized UHMW-PE samples in air and nitrogen atmosphere with various dosages D of electron beam irradiation.

D / kGy	M_w / kg · mol^{-1}			
	stabilized samples		unstabilized samples	
	nitrogen	air	nitrogen	air
10	1,640	1,280	445	416
17	1,000	900	433	408
22	900	740	315	328
100	213	125	59	87

Conclusions

Ultra-high molar mass polyethylene undergoes crosslinking and molecular degradation during sintering and irradiation, depending on the absorbed dosage. In nitrogen atmosphere the crosslinking process predominates over molecular degradation whereas in air the extent of degradation is remarkable increased. α-Tocopherol is an efficient radical scavenger which partially prevents UHMW-PE from being degraded during sintering and irradiation but also reduces the extent of crosslinking.

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