J Mater Sci: Mater Med (2006) 17:1333–1340
DOI 10.1007/s10856-006-0608-6

Accelerated ageing experiments with crosslinked and conventional ultra-high molecular weight polyethylene (UHMW-PE) stabilised with α-tocopherol for total joint arthroplasty

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Received: 17 May 2005 / Accepted: 24 October 2005

Abstract Samples of untreated ultra-high molecular weight polyethylene (UHMW-PE), UHMW-PE sterilized with γ-rays in nitrogen atmosphere (conventional UHMW-PE, widely used for articulating surfaces in endoprostheses) and UHMW-PE, which has been crosslinked by electron beam irradiation and annealed subsequently, were stabilized with α-tocopherol and aged in air at 120°C as well as in 10% aqueous hydrogenperoxide with 0.04 mg/ml $FeCl_3$ as catalyst at 50°C. The oxidative degradation was monitored with the help of infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), solubility measurements and size exclusion chromatography (SEC) and were compared to unstabilized samples. When aged in air at 120°C, the crosslinked UHMW-PE showed a slightly slower increase of the carbonyl (CO)-number (according to DIN 53383) in FTIR than conventional UHMW-PE. A stabilisation with 0.4% w/w α-tocopherol resulted in an increase of lifetime by a factor of approx. 40 for all samples. Ageing in 10% aqueous H_2O_2 at 50°C yielded similar results for all three unstabilised samples. The addition of the natural antioxidant α-tocopherol led to a prolongation of lifetime by a factor of approx. 2.5. A linear loss of α-tocopherol was detected during ageing. An increase of crystallinity as well as lamella thickness during ageing was observed with the help of DSC. The two-phase structure of crosslinked UHMW-PE with two melting endotherms at 114°C and 137°C was replaced very quickly by a single melting point at 130°C. This effect was delayed with the stabilized samples. In the solubility and SEC measurements, a severe molecular degradation and drop of molar mass of all materials could be observed after ageing in H_2O_2, leading to a complete destruction and, in case of crosslinked UHMW-PE, to a serious damage of the molecular network, respectively.

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1 Introduction

Since the 1960's, ultra-high molecular-weight polyethylene (UHMW-PE) has been used successfully as a material for articulating surfaces in medical implants, especially for cups in hip endoprostheses. Lately, UHMW-PE, which has been crosslinked by electron beam irradiation and annealed subsequently, has entered the market as a new promising material for this application. In literature, investigations showing the wear resistance of crosslinked UHMW-PE to be fundamentally higher than the wear resistance of standard UHMW-PE are predominant. Although clinical long-time studies are not available yet due to the novelty of the material, this fact could prolong the lifetime of endoprostheses considerably and lower the risk of an incidence of osteolysis caused by wear particles in the surroundings of the prosthesis. The formation of wear particles followed by osteolysis is considered to be one of the main reasons for failure of conventional UHMW-PE hip cups. Hip simulator tests proved the crosslinked material to possess a considerable higher wear resistance than standard UHMW-PE [1–10].

Investigations on the long-term stability showed that crosslinked UHMW-PE is less degraded by an oxidative

attack than standard UHMW-PE [2–4, 7, 10]. In the case of not crosslinked, conventional UHMW-PE, the oxidation process is initiated during processing and γ-ray sterilisation of the material and continues in-vivo. Free radicals are produced due to bond scission especially in the irradiation step or are already present in the human body such as hydroxy-radicals. In the presence of oxygen, the O_2 molecules react with these radicals and form peroxides, which accelerates the oxidation and leads to a chain-scission of the polyethylene-backbone. As a result of this break, the molar mass of the UHMW-PE is lowered. Due to the higher mobility of the shorter polyethylene-chains formed by chain scission, the crystallinity as well as the density increases, which causes an embrittlement of the material. All this leads to an enhanced formation of polyethylene-debris by the articulating action of the joint [11–28].

The better long-term performance of crosslinked UHMW-PE is attributed in the first place to the annihilation of free radicals which are formed during irradiation [29, 30]. This is done by excluding oxygen during irradiation and annealing the material after the irradiation step. In the annealing process, the UHMW-PE samples are stored at a temperature above the melting point for approx. 2 h in an inert atmosphere. This allows the remaining free radicals to recombine resulting in a further increase of the network density. After the annealing process, no further incidence of free radicals can be found in the UHMW-PE samples [31, 32].

However, when regarding the chemical structure of crosslinked UHMW-PE from a critical point of view, an enhanced tendency for oxidation can be expected due to the high density of tertiary C-H bonds in crosslinked UHMW-PE, which are known to be highly sensitive to an oxidative attack.

In literature, the first choice of accelerated ageing method is often that of the use of gaseoux oxygen, which acts as an oxidiser [33], (FDIS ISO 5834-3). Though these methods are well accepted among the experts for simulating shelf-ageing, it is questionable whether they are suited properly to simulate the oxidative challenge in an aqueous environment as it exists in-vivo. According to literature, a so-called "metabolic burst" can take place in the surroundings of implants causing an enhanced formation of hydrogenperoxide, which is assumed to be one driving force of oxidation in-vivo [12, 34, 35]. Therefore, in this study accelerated ageing experiments are carried out applying oxidative stress on crosslinked as well as conventional UHMW-PE by means of gaseous oxygen as well as aqueous hydrogenperoxide.

Several investigations proved the suitability of α-tocopherol as a stabilizer for conventional UHMW-PE used for endoprostheses [36–38]. Adding α-tocopherol may prolong the lifetime of such endoprostheses by a factor of 3 to 5. The biocompatibility tests are at an advanced stage [39–41], clinical studies are in preparation. Recently, a new method made it possible to apply the stabilisation with α-tocopherol to crosslinked UHMW-PE as well [42]. The ageing tests in this study will include specimens made of crosslinked UHMW-PE stabilised with α-tocopherol, in order to evaluate the suitability of α-tocopherol as a stabilizer for crosslinked UHMW-PE.

The oxidative degradation of the specimens will be monitored by means of infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and size exclusion chromatography (SEC).

2 Materials and methods

2.1 Preparation and processing of the UHMW-PE-specimens

UHMW-PE was Hostalen GUR 1020 from TICONA AG (Frankfurt/Main Germany), which fulfils the requirements of ISO 5834 Part 1 and 2 (Implants for surgery—UHMW-PE powder and moulded forms). For the accelerated ageing experiments, UHMW-PE stabilised with 0.4% α-tocopherol was used. The α-tocopherol was added to the polymer powder before processing [36]. The powder was sintered to disks (diameter = 600 mm, thickness = 60 mm) at 220°C and 35 bar for 7 h. From these discs, cubes ($20 \times 20 \times 20$ mm^3) were cut out. Half of the specimens were sterilised with γ-irradiation at a dose of 25 kGy under nitrogen atmosphere according to standard procedures for artificial hip-cups. Crosslinked UHMW-PE was Durasul® from Zimmer, Inc. (former Centerpulse Ltd. and Sulzer Medica respectively, Winterthur, Switzerland). This material is crosslinked by electron beam irradiation (10 MeV) at a dose of 100 kGy, annealed under inert atmosphere for 2 h at temperatures above the melting point and sterilised with ethyleneoxide subsequently.

For the stabilisation of crosslinked UHMW-PE, a new method was developed (patent pending), adding the α-tocopherol to the final product just before the sterilization with ethyleneoxide. At the moment of the accelerated ageing experiments, only a mass content of approx. 1.6% α-tocopherol could be realised; tests with lower α-tocopherol content are in preparation. Details on the stabilisation methodology can be found in [42]. The used sample codes are listed in Table 1.

For the tests, thin films ($20 \times 20 \times 0.2$ mm^3) were cut off the cubes with the help of a microtome cutter.

2.2 Accelerated ageing experiments

All films were threaded onto a silver wire with fixed distances between each other like on a clothesline. For the accelerated ageing in air, the wires were fixed in an oven at 120°C in air following DIN 53383. Concerning the ageing in an aqueous

Table 1 Sample codes of the UHMW-PE polymer films

PE-unster.-unstab.	Sintered UHMW-PE, unsterilized	Without α-tocopherol
PE-ster.-unstab.	UHMW-PE, sterilized with γ-irradiation at 25 kGy under nitrogen atmosphere	Without α-tocopherol
PE-xlinked-unstab.	UHMW-PE, crosslinked by electron beam irradiation at 100 kGy and annealed subsequently	Without α-tocopherol
PE-unster.-stab.	Sintered UHMW-PE, unsterilized	With 0.4% w/w α-tocopherol
PE-ster.-stab.	UHMW-PE, sterilized with γ-irradiation at 25 kGy under nitrogen atmosphere	With 0.4% w/w α-tocopherol
PE-xlinked-stab.	UHMW-PE, crosslinked by electron beam irradiation at 100 kGy and annealed subsequently	With approx. 1.6% w/w α-tocopherol

environment, the wires were placed in vessels containing 10% aqueous H_2O_2 with 0.04 mg/ml $FeCl_3$ as catalyst and stored in an oven at 50°C. The aqueous H_2O_2 solutions were changed in timed intervals of 5 days.

For the FTIR measurements, the samples were taken out of the oven and H_2O_2 solution respectively, cleaned, placed in the spectrometer and put back immediately after the measurement was done. For all the other tests, appropriate pieces were cut off from the specimens at timed intervals.

2.3 Fourier transform infrared spectroscopy (FTIR)

The degree of oxidation of the UHMW-PE films (five films per sample) was investigated with the help of FTIR spectroscopy. A Perkin Elmer® Spectrum One spectrometer was used to measure the carbonyl number (CO-number) of the films according to DIN 53383 (Resolution: 1 cm^{-1}, 4 scans per spectrum). The CO-number is the ratio of the absorbance at 1718 ± 15 cm^{-1} (carbonyl group) to the absorbance at 2020 ± 20 cm^{-1} (C-H vibration) and directly linked to the extent of the oxidative degradation.

Mapscans were carried out in order to investigate the homogeneity of oxidation using a Perkin Elmer® AutoImage FTIR-microscope connected to the Perkin Elmer® Spectrum One scanning the whole area of a specimen with a grid distance of 200 × 200 μm^2 (aperture size 100 × 100 μm^2). The peak area instead of the height was used to calculate the CO-number in the mapscan. All spectra were collected in transmission.

The α-tocopherol concentration was determined by the ratio of the area of the α-tocopherol-peak at 1265 cm^{-1} to the area of the PE-peak at 2020 cm^{-1}.

2.4 DSC-analysis

DSC analysis was carried out with a Perkin Elmer® DSC 7. Approx. 10 mg were heated from 50°C to 190°C, cooled down and heated up to 190°C again under nitrogen atmosphere at a heating and cooling rate of 10°C per minute. The melting point as well as crystallinity were determined by calculating the peak maxima and the peak area, respectively (100% crystallinity corresponds to a specific melting enthalpy of 290 J/g according to Polymer Handbook, 3rd edition). Furthermore, the distribution of lamellae thickness was calculated according to Thompson [43] using data from the second heating run, according to their equation

$$T_m = T_m^0 \cdot \left(1 - \frac{2 \cdot \sigma_e}{D_g \cdot \Delta H_k^\infty}\right)$$

with T_m^0 melting point of an infinite cristal (PE-HD: 145, 5°C)

T_m melting point of a cristal with thickness D_g
ΔH_k^∞ specific melting enthalpy of an infinite cristal (PE-HD: 290 J/cm^3)
σ_e specific surface energy of a lamellae (PE-HD: 90 mJ/m^2)

Since we were mainly interested in the morphological changes during ageing and not in absolute numbers, neither a correction according to Crist and Mirabella [44] nor an extrapolation to a heating rate of 0°C/min [45] was carried out.

2.5 Size exclusion chromatography (SEC) and determination of solubility

The molecular weight distributions of the samples were determined at 135 ± 0.02°C with the "GPC 220" chromatograph of Polymer Laboratories (Church Stretton, UK) equipped with a differential refractive index detector (DRI) and a differential viscosimeter 210 R from Viscothek (Houston, Texas, USA). A set of two identical columns was used, packed with crosslinked styrene-divinylbenzene (PLGel Mixed-A LS, particle size: 20 μm, length: 300 mm, inner diameter:

7.5 mm, from Polymer Laboratories (Church Stetton, UK). 1,2,4-Trichlorobenzene (Merck, Darmstadt, Germany) containing 0.0125% (w/v, mixed at room temperature) 2,6-di-tert.-butyl-(4-methylphenol) (BHT) was used as solvent and as eluent. Prior to entering the pump, the solvent was degassed with an online degasser PL-DG2 (Erc Inc., Kawaguchi City, Japan). The flow rate was set to 0.2 ml/min to avoid molecular degradation of the high molecular weight fractions [46].

The solubility was first estimated roughly in pilot tests. The polymer solutions were then prepared in 10 ml of the solvent with mass fractions resulting in a concentration of the soluble fraction of approximately 1 mg/ml. After flushing with pure nitrogen for 15 min, the samples were placed in an oven and rolled at about 3 rpm at 150°C for 5 h prior to injection. This procedure homogenises the samples with negligible mechanical stress.

The insoluble fractions of the polymer were filtered off and dried in air for 5 h at 150°C. The gel content was determined gravimetrically as well as via measuring the area of the DRI signal, which is proportional to the sample concentration. The final soluble fraction resulted from the mean value of both data.

3 Results

3.1 FTIR spectroscopy

Figure 1 shows the results of the accelerated ageing tests at 120°C in air of unstabilized specimens. In accordance with literature, the crosslinked UHMW-PE performs better than the γ-sterilized, conventional UHMW-PE, a fact which can be contributed in first place to the annealing under inert atmosphere and the saturation of free radicals. However, crosslinked UHMW-PE is oxidised faster than unsterilised UHMW-PE, which may suggest an increased sensitivity of the crosslinked points to oxidative attack.

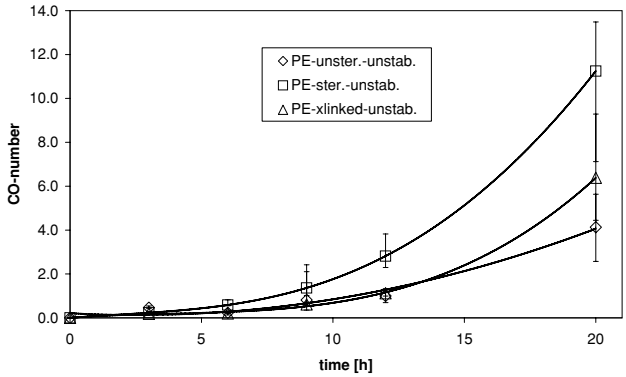

Fig. 1 Accelerated ageing of unstabilized UHMW-PE samples in air at 120°C.

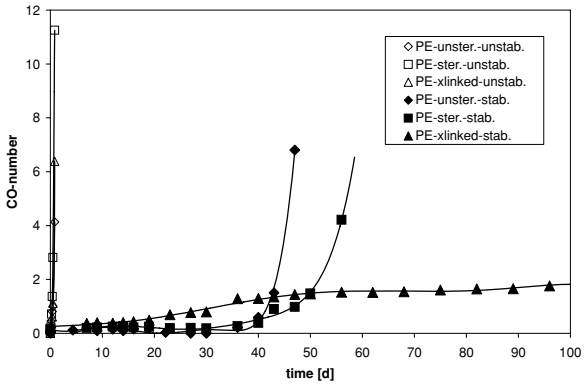

Fig. 2 Accelerated ageing of stabilized and unstabilized samples in air at 120°C (note: stabilizer content of PE-xlinked-stab.: 1.6%, all others: 0.4%).

In Fig. 2, the tremendous effect of a stabilisation with α-tocopherol can be seen. The lifetime is prolongated by a factor of 40 when ageing in air is applied. The stabilized, crosslinked UHMW-PE could not be oxidised within the duration of measurement. This fact is caused by the higher stabilizer content of 1.6% w/w compared to 0.4% w/w of the other samples, as explained in part 1. With the same mass content of α-tocopherol, a similar lifetime may be expected (will be investigated).

All specimens aged in air showed an inhomogeneity regarding their oxidative degradation. During the experiments, a zone of highly oxidised material was formed along the edges of the films. Although we tried to measure within the less oxidised zones this caused a rather high scattering of the data. Figure 3 shows a picture as well as a FTIR map scan of a film after the ageing experiments.

No inhomogeneities were observed when accelerated ageing in aqueous H_2O_2 was applied. As can be seen in Fig. 4, all unstabilised samples show similar oxidative degradation, differences are within accuracy of measurement. A repetition of the experiments at 60°C and higher H_2O_2 concentration yielded the same results. Stabilisation with α-tocopherol resulted in a lifetime prolongation of approx. 2.5. Similar to the tests in air, the stabilised, crosslinked sample could not be oxidised due to its high amount of stabilizer of 1.6% w/w compared to 0.4% w/w. With the same amount of α-tocopherol, a similar lifetime may be expected.

The loss of α-tocopherol was observed during the ageing experiments in aqueous H_2O_2 (see Fig. 5). The α-tocopherol content decreased continuously while no oxidation can be monitored. The stabilizer inhibits oxidative attacks and is used up in this process. A comparison with Fig. 4 shows that oxidation starts before all stabilizer is consumed, which can also be seen in Fig. 5 in a slight decrease of the slope of the curves or even better in Fig. 6, where the α-tocopherol content is plotted versus the CO-number. The α-tocopherol is no longer able to completely suppress oxidation but is still

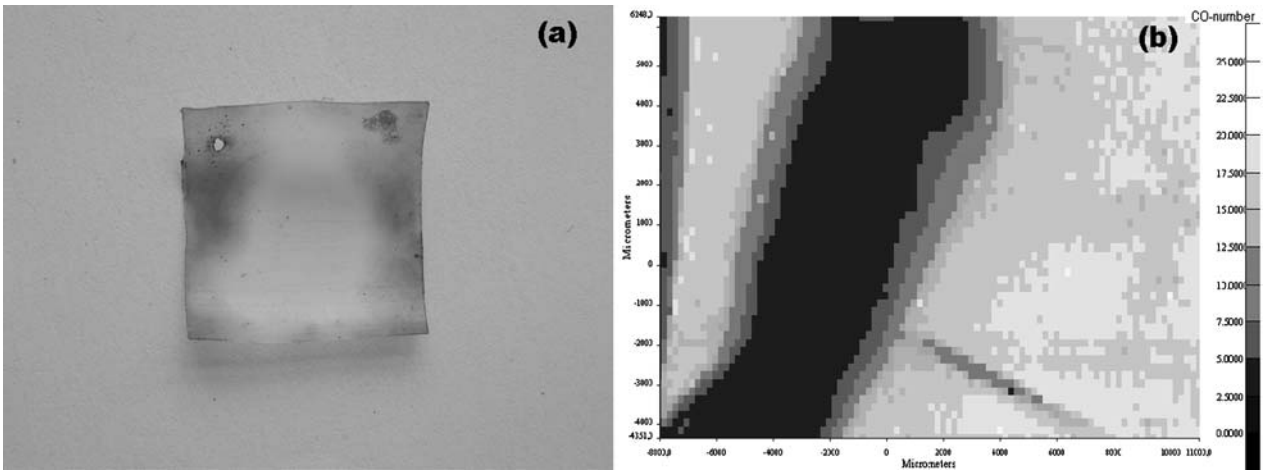

Fig. 3 Inhomogeneous oxidation of a UHMW-PE film (PE-unster.-unstab.) after 40 h accelerated ageing in air at 120°C: the darker parts are highly oxidised (a). On the right (b): FTIR-mapscan of a part of the surface(area: 20 × 10.6 mm^2 of 20 × 20 mm^2, centered).

active. This fact is also considered to be responsible for the nearly linear increase of the CO-number after 80 days, in contrast to the expected exponential function of oxidative degradation for polymer materials, which can be observed with the unstabilised samples in Fig. 4.

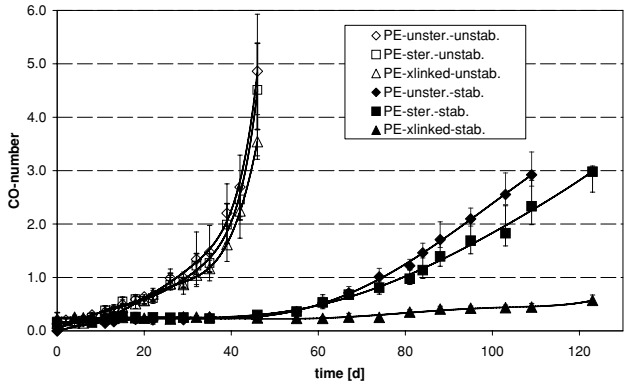

Fig. 4 CO-number vs. storage time in 10% aqueous H_2O_2 at 50°C. (note: stabilizer content of PE-xlinked-stab.: 1.6%, all others: 0.4%).

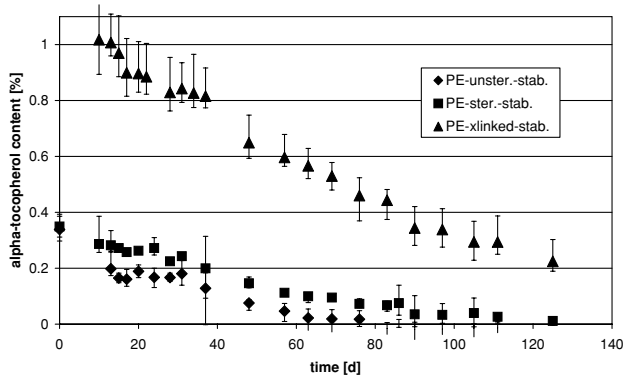

Fig. 5 The loss of α-tocopherol during the ageing experiments in aqueous H_2O_2 at 50°C.

No data could be found on the desorption behaviour of α-tocopherol in UHMW-PE in an aqueous environment at 50°C. Data was only available from desorption experiments of conventional UHMW-PE-films stabilised with α-tocopherol in fetal bovine serum (FBS) at 37°C and 60°C (unpublished experiments). An estimation concerning the loss of α-tocopherol based on these data and the formula of Crank and Park [47] for desorption from an infinite plate yielded a loss of approx. 45% after 120 days due to diffusion from films with a thickness of 200 μm at 50°C. Thus, an even better stabilisation effect can be expected when ageing bulk material, where the loss of α-tocopherol due to diffusion may be neglected. Assuming the articulating surface of a hip- or knee-endoprosthesis to be a plate with thickness 1 cm, a loss of approx. 4% of α-tocopherol may be expected after 20 years at 37°C.

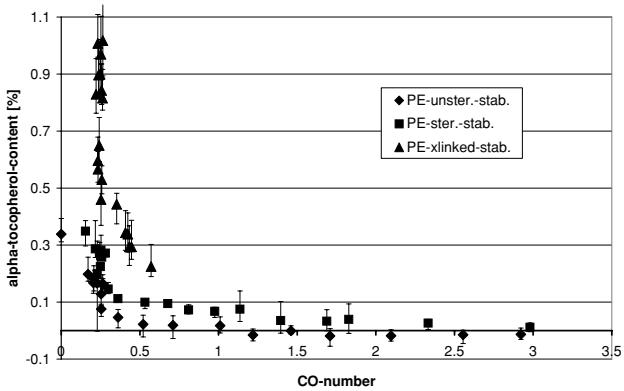

Fig. 6 The loss of α-tocopherol during the ageing experiments in aqueous H_2O_2 at 50°C plotted versus the oxidative degradation (CO-number).

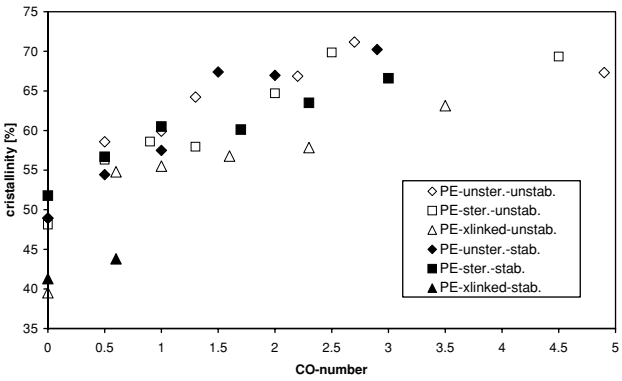

Fig. 7 Increase of crystallinity in UHMW-PE films due to oxidative degradation (aged in aqueous H_2O_2 at 50°C).

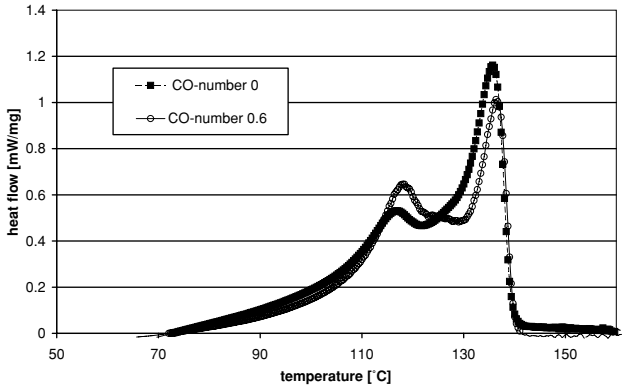

Fig. 9 Changes of melting behaviour of crosslinked UHMW-PE stabilised with α-tocopherol (PE-xlinked-stab.) after ageing in aqueous H_2O_2 (DSC-plot).

3.2 DSC-measurements

The samples aged in H_2O_2 were investigated with the help of DSC-measurements. Due to the molecular degradation caused by the oxidation and the higher mobility of the now shorter chains, the crystallinity of all samples increased with ageing (see Fig. 7). At a CO-number of approx. 2, no further increase could be observed.

The average lamellae thickness (in the order of magnitude of 20 nm, experimental error ±0.8 nm) also went up during ageing. It reached its maximum at a CO-number of 1 to 1.5 and then decreased slightly again. This effect was stronger with unstabilized samples (changes up to 6 nm), the stabilized samples only showed small changes in lamellae thickness (up to 3 nm).

The largest changes were observed with unstabilised crosslinked UHMW-PE. Crosslinked UHMW-PE is irradiated at elevated temperatures (approx. 100°C) resulting in a two phase structure with two melting endotherms at 114°C and 137°C [48]. This two-phase structure diminished very quickly during ageing (see Fig. 8). Even at a CO-number of 0.6, the two melting peaks were replaced for the most part by one melting peak at approx. 130°C. This effect could not be observed with the stabilized sample, where only small changes in DSC at a CO-number of 0.6 were detected (Fig. 9). Unfortunately, no further oxidation could be applied to the material due to the high stability of PE-xlinked-stab. (caused by the α-tocopherol content of 1.6%, see part 1), as experiments were stopped after 123 days.

3.3 Size exclusion chromatography (SEC) and determination of solubility

All experiments were carried out with the samples aged in aqueous H_2O_2. Unstabilised conventional UHMW-PE for hip cups is already largely crosslinked due to sintering and sterilization with γ-rays (see Fig. 10). The solubility drops to 44% after sintering and to 20% after sterilisation, respectively. Adding the radical scavenger α-tocopherol partially inhibits this crosslinking (see also [49]).

During the ageing process (all samples were aged up to a CO-number of approx. 5, except for the stabilized crosslinked

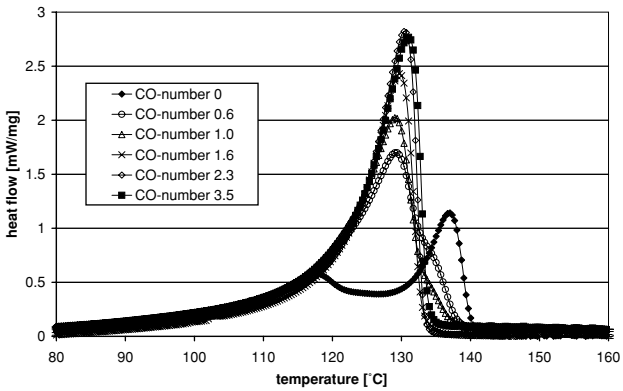

Fig. 8 Changes of melting behaviour of unstabilised crosslinked UHMW-PE (PE-xlinked-unstab.) after ageing in aqueous H_2O_2 (DSC-plot).

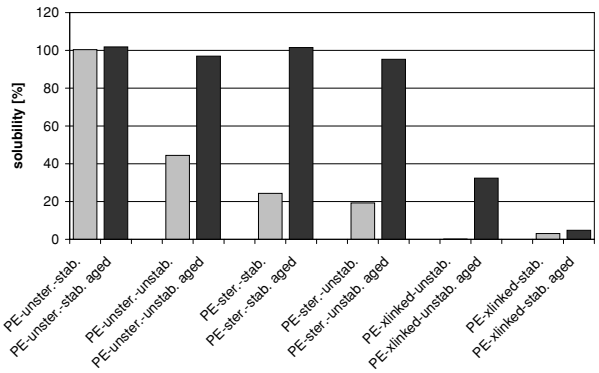

Fig. 10 Solubility of all samples prior to and after ageing (all samples aged to CO-number of approx. 5, except for PE-xlinked-stab., which could be aged only to a CO-number of 1.3 within duration of measurement).

Table 2 Molar masses of the soluble fractions of the UHMW-PE samples prior to and after ageing in 10% aqueous H_2O_2 at 50°C, determined by means of size exclusion chromatography

	Universal calibration for PE-HD using $K = 4.06 * 10^{-4}$ dl/g, $a = 0.725$		Universal calibration with online viscosity detector	
	Mw [kg/mol]	Mn [kg/mol]	Mw [kg/mol]	Mn [kg/mol]
PE-unster.-unstab.	492	135	646	155
PE-unster.-unstab. aged	56	10.7	68	15
PE-unster.-stab.	1016	190	1230	149
PE-unster.-stab. aged	170	23	230	24.6
PE-ster.-stab.	214	76	402	92
PE-ster.-stab. aged	203	27	341	31
PE-ster.-unstab.	94.5	42	128	59
PE-ster.-unstab. aged	52	9	75	13.5
PE-xlinked-unstab.	12.4	8	Visco-signal too weak	Visco-signal too weak
PE-xlinked-unstab. aged	40	12	57.5	11
PE-xlinked-stab.	18.7	11.7	Visco-signal too weak	Visco-signal too weak
PE-xlinked-stab. aged	18	11.5	Visco-signal too weak	Visco-signal too weak

UHMW-PE, which only reached a CO-number of 1.3), the network is destroyed, as can be seen in Fig. 10. For all samples except for the highly crosslinked UHMW-PE, the solubility rises to 100% after ageing. The solubility of the unstabilised crosslinked sample increases from nearly 0 to 32%.

The severe molecular degradation of the material due to oxidation could also be observed in size exclusion chromatography (see Table 2). The drop of molar mass of the soluble fraction is significant for most samples except for crosslinked UHMW-PE, whose molar mass increased. Considering the fact that only the soluble fraction is accessible to size exclusion chromatography, this is not surprising. Beside the drop of molar mass due to chain scission, a destruction of the molecular network releases bigger molecules causing an increase of molar mass. The first effect strongly dominates for conventional UHMW-PE as can be seen in Table 2, where the wide-meshed network is completely destroyed and the molecular chains are heavily degraded. Regarding the unstabilised crosslinked UHMW-PE, the majority of the molecules are still crosslinked (68%), although crosslink density probably decreased significantly.

The data was evaluated in two ways: in the first method, a calibration curve for polystyrene standards was determined and converted in a calibration curve for PE-HD using universal calibration with K and a values for polystyrene and PE-HD, respectively (polystyrene: $K = 1.75 * 10^{-4}$ dl/g, $a = 0.67$; PE-HD: $K = 4.06 * 10^{-4}$ dl/g, $a = 0.725$). In the second method, a universal calibration curve ($\log(M^*[\eta])$) was determined with polystyrene standards. The molar masses of the UHMW-PE samples were then calculated via universal calibration with the help of the online viscosity detector.

The first method is only applicable to linear molecules, while universal calibration with an online viscosity may also evaluate branching. Both results would only be the same for linear PE-HD. The second method always yielded higher values for Mw, indicating the molecules to be branched to a varying degree, as expected after the crosslinking and sterilisation process, respectively.

4 Conclusion

The in-vivo-oxidative degradation of conventional UHMW-PE for articulating surfaces of endoprostheses is widely accepted in literature (see part 1). A stabilisation with α-tocopherol can delay this damage significantly. Crosslinked UHMW-PE, which distinguishes itself by its high wear resistance, shows a slightly lower degradation rate when aged in air but similar degradation rate when aged in aqueous H_2O_2 to the conventional material. Although its molecular network is not completely destroyed during ageing, it is heavily damaged. Since the high wear resistance of crosslinked UHMW-PE is primarily based on its network structure, this fact could eventually lead to a loss of its superior wear performance. A stabilisation with α-tocopherol can prevent this degradation and, combined with the excellent wear resistance of crosslinked UHMW-PE, can lead to a remarkable long lifetime of total joint endoprostheses equipped with an articulating surface made of crosslinked UHMW-PE stabilized with α-tocopherol.

Acknowledgments We like to thank DI W. Schneider and Dr. M. Windler of Zimmer, Inc. (former Centerpulse Ltd.), Winterthur, Switzerland, for preparation of specimens as well as Dr. Ernst Wagner from Hoffmann-LaRoche AG, Grenzach-Wyhlen, Germany, for providing the α-tocopherol as gift samples.

References

1. A. S. GREENWALD, T. W. BAUER and M. D. RIES in the *67th annual meeting of the American Academy of Orthopaedic Surgeons*, March 2000, Orlando, Florida.

2. M. T. MANLEY, W. N. CAPELLO, J. A. D'ANTONIO and A. A. EDIDIN in the *67th annual meeting of the American Academy of Orthopaedic Surgeons*, March 2000, Orlando, Florida.
3. O. K. MURATOGLU, C. R. BRAGDON, D. O. O'CONNOR and W. H. HARRIS in the *46th annual meeting of the Orthopaedic Research Society*, March 2000, Orlando, Florida.
4. C. R. BRAGDON, D. O. O'CONNOR, O. K. MURATOGLU and W. H. HARRIS in the *45th annual meeting of the Orthopaedic Research Society*, February 1999, Anaheim, California.
5. O. K. MURATOGLU, D. O. O'CONNOR and W. H. HARRIS in the *45th annual meeting of the Orthopaedic Research Society*, February 1999, Anaheim, California.
6. H. A. MCKELLOP, F. W. SHEN and R. SALOVEY in the *43th annual meeting of the Orthopaedic Research Society*, February 1997, San Francisco, California.
7. V. K. POLINENI, A. WANG and J. H. DUMBLETON, *ASTM Spec. Tech. Publ., STP 1307 (Characterization and Properties of UHMWPE)* (1998) 95.
8. R. CHIESA, M. C. TANZI, S. ALFONSI et al., *J. Biomed. Mater. Res.* **50** (2000) 381.
9. H. OONISHI, H. ISHIMARU and A. KATO, *J. Mater. Sci.: Mater. Med.* **7** (1996) 753.
10. S. M. KURTZ, O. K. MURATOGLU, M. EVANS and A. A. EDIDIN, *Biomat.* **20** (1999) 1659.
11. M. GOLDMAN, R. GRONSKY, R. RANGANATHAN and L. PRUITT, *Polymer* **37** (1996) 2909.
12. P. EYERER, *Kunststoffe* **77** (1987) 617.
13. F. J. BUCHANAN, B. SIM and S. DOWNES, *Plast., Rub. and Comp. Proc. and Appl.* **27** (1998) 148.
14. E. S. GROOD, R. SHASTRI and C. N. HOPSON, *J. Biomed. Mat. Res.* **16** (1982) 399.
15. J. A. DAVIDSON and G. SCHWARTZ, *J. Biomed. Mat. Res.: Appl. Biomat.* **21** (1987) 261.
16. B. ZICAT, C. A. ENGH and E. GOKCEN, *J. Bone a. Joint Surg.* **77A** (1995) 432.
17. M. GOLDMAN, R. GRONSKY, G. LONG and L. PRUITT, *Poly. Deg. and Stab.* **62** (1998) 97.
18. M. DENG and S. W. SHALABY, *J. Appl. Polym. Sci.* **58** (1995) 2111.
19. J. L. HENRY, L. R. ASCENION and A. GARTON, *J. Polym. Sci.: Polym. Chem.* **30** (1992) 1693.
20. E. BRACH DEL PREYER, M. CROVA, L. COSTA, A. DALLERA, G. CAMINO and P. GALLINARO, *Biomat.* **17** (1996) 873.
21. L. COSTA, M. P. LUDA, L. TROSSARELLI, E. M. BRACH DEL PREYER, M. CROVA and P. GALLINARO, *Biomat.* **19** (1998) 659.
22. L. COSTA, M. P. LUDA, L. TROSSARELLI, E. M. BRACH DEL PREYER, M. CROVA and P. GALLINARO, *Biomat.* **19** (1998) 1371.
23. M. GOLDMAN, M. LEE, R. GRONSKY and L. PRUITT, *J. Biomed. Mat. Res.* **37** (1997) 43.
24. R. M. ROSE, E. V. GOLDFARB, E. ELLIS and A. N. CRUGNOLA, *J. Orthop. Res.* **2** (1984) 393.
25. V. PREMNATH, A. BELLARE, E. W. MERILL, M. JASTY and W. H. HARRIS, *Polym.* **40** (1999) 2215.
26. S. O. HAN, D. W. LEE and O. H. HAN, *Polym. Degrad. Stab.* **63** (1999) 237.
27. A. SINGH, *Radiat. Phys. Chem.* **56** (1999) 375.
28. B. YEOM, Y. J. YU, H. A. MCKELLOP and R. SALOVEY, *J. Polym. Sci. A: Polym. Chem.* **36** (1998) 329.
29. C. BIRKINSHAW, J. J. LEAHY and R. BARKLIE, *Polym. Degrad. Stab.* **63** (1999) 31.
30. V. PREMNATH, W. H. HARRIS, M. JASTY and E. W. MERRILL, *Biomat.* **17** (1996) 1741.
31. Y. IKADA *et al., J. Polym. Sci. A: Polym. Chem.* **37** (1999) 159.
32. P. O'NEILL, C. BIRKINSHAW, J. J. LEAHY and R. BARKLIE, *Polym. Degrad. Stab.* **63** (1999) 31.
33. W. M. SANFORD and K. A. SAUM in the *41st Annual Meeting of the Orthopaedic Research Society*, Orlando, 1995.
34. H. TSCHESCHE and H. W. MCCARTNEY, *Eur. J. Biochem.* **120** (1981) 183.
35. K. YOSHIO and E. NIKI, *Degrad. Stab. Polym.* **1** (1983) 337.
36. C. WOLF, T. KRIVEC, J. BLASSNIG, K. LEDERER and W. SCHNEIDER, *J. Mat. Sci.: Mat. In Med.* **13** (2002) 185–189.
37. S. AL-MALAIKA, C. GOODWIN, S. ISSENHUTH and D. BURDICK, *Polym. Deg. Stab.* **64** (1999) 145.
38. S. AL-MALAIKA, H. ASHLEY and S. ISSENHUTH, *J. Polym. Sci. Part A: Polym. Chem.* **32** (1994) 3099.
39. C. WOLF, K. LEDERER and U. MÜLLER, *J. Mat Sci.: Mat in Med.* **13** (2002) 701.
40. C. WOLF, K. LEDERER, R. PFRAGNER, K: SCHAUENSTEIN, *J. Mat Sci.: Mat in Med.*, in prep.
41. C. WOLF, K. LEDERER, H. BERGMEISTER, U. LOSERT, P. BÖCK, *J. Mat Sci.: Mat in Med.*, submitted.
42. C. WOLF, J. MANINGER and K. LEDERER, *J. Mat Sci.: Mat in Med.*, in prep.
43. W. THOMSON, *Philos. Mag.* **42** (1871) 448.
44. B. CRIST and F. M. MIRABELLA, *J. Polym. Sci B.: Polym. Phy.* **37** (1999) 3131–3140.
45. K. H. ILLERS and H. HENDUS, *Makrom. Chem.* **113** (1968) 1–22.
46. N. AUST, M. PARTH and K. LEDERER, *Int. J. Polym. Anal. Charact.* **6** (2001) 245.
47. J. CRANK and G. S. PARK, in "Diffusion in Polymers" (Academic Press, London and New York, 1968) p.15.
48. O. K. MURATOGLU, C. R. BRAGDON, D. O. O'CONNOR and W. H. HARRIS, *25th annual meeting of the Society for Biomaterials*, (1999).
49. M. PARTH, N. AUST, K. LEDERER, *J. Mat. Sci.: Mat. In Med.* **13** (2002) 917–921.