J Mater Sci: Mater Med (2006) 17:1323–1331
DOI 10.1007/s10856-006-0607-7

Stabilisation of crosslinked ultra-high molecular weight polyethylene (UHMW-PE)-acetabular components with α-tocopherol

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Received: 17 May 2005 / Accepted: 24 October 2005

Abstract A stabilisation of crosslinked ultra-high molecular weight polyethylene (UHMW-PE) with α-tocopherol (vitamin E) used for endoprostheses can increase its resistance against oxidative degradation remarkably. However, the method used for conventional UHMW-PE of adding α-tocopherol to the UHMW-PE powder before processing can not be applied for crosslinked UHMW-PE, since the α-tocopherol hinders the crosslinking process, which would be accompanied by a heavy degradation of this vitamin. The α-tocopherol has therefore to be added after the crosslinking process. This paper presents two methods for a stabilisation of finished products with α-tocopherol. In method 1, UHMW-PE-cubes ($20 \times 20 \times 20\,mm^3$) were stored in pure α-tocopherol under inert atmosphere at temperatures from 100°C to 150°C resulting in a high mass fraction of α-tocopherol in the edge zones. For further homogenisation, the cubes were stored in inert atmosphere at temperatures from 160°C to 200°C. In method 2, supercritical CO_2 was used to incorporate the vitamin into the UHMW-PE. In an autoclave vessel, the cubes were treated with α-tocopherol dissolved in supercritical CO_2 for several hours at temperatures from 100°C to 170°C. In both cases, the mass fraction of α-tocopherol was detected with the help of a FTIR-microscope. Both methods are well suited to stabilise crosslinked UHMW-PE with α-tocopherol. A stabilisation of the sensitive edge layer as well as a nearly homogenous distribution with varying α-tocopherol content may be realised by varying the process parameters. Using method 2, standard hip cups were stabilized nearly homogeneously with varying mass fraction of α-tocopherol. No oxidation of the UHMW-PE could be detected by infrared spectroscopy (FTIR) and HPLC studies showed a very low degradation of the α-tocopherol for both processes.

1 Introduction

Approx. 70% of all hip- and knee-endoprostheses worldwide are equipped with articulating surfaces made of ultra-high molecular weight polyethylene (UHMW-PE). Although UHMW-PE has been used successfully for more than 30 years now in this field of application, its lifetime is often limited to 10 to 15 years due to an oxidative degradation *in vivo* [1–18]. This degradation can be delayed remarkably by adding the natural antioxidans α-tocopherol (vitamin E) to the UHMW-PE [19–21]. The biocompatibility tests of this new compound are at an advanced stage [22–24], clinical studies are in preparation.

Lately, a material has gained more and more importance for articulating surfaces in endoprostheses, namely crosslinked UHMW-PE, a consequential further development of conventional UHMW-PE. This UHMW-PE is crosslinked by electron beam irradiation and annealed

[§]In partial fulfilment of a Ph.D. (Dr.mont.) thesis at the University of Leoben

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subsequently. The network structure produced by this treatment leads to an improved wear resistance. Especially hip simulator tests proved the crosslinked material to possess a considerable higher wear resistance than standard UHMW-PE [25–34].

In the annealing process, the UHMW-PE samples are stored at a temperature above the melting point for several hours in an inert atmosphere. This allows the remaining free radicals to recombine resulting in a further increase of the network density. Since the free radicals are considered to be the main driving force in oxidative degradation, the annihilation of free radicals also improves the long-term stability of crosslinked UHMW-PE [26–28, 31, 34].

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 concentration of tertiary C-H bonds, which are known to be highly sensitive to an oxidative attack. Accelerated ageing tests in an aqueous environment (aqueous hydrogen peroxide) have shown that the crosslinked material is degraded similar to conventional UHMW-PE and a stabilisation of crosslinked UHMW-PE with α-tocopherol leads to an impressive increase of its resistance against oxidation [35].

However, it is not possible to add the α-tocopherol to the UHMW-PE powder before any processing is applied like it is done with conventional UHMW-PE [19, 36, 37]. α-Tocopherol acts as a radical scavenger, hindering the crosslinking process and leading to a material with a much lower network density followed by a lower wear resistance. Furthermore, most of the α-tocopherol is degraded during the crosslinking irradiation resulting in a poorly protected material with low mass fraction of α-tocopherol but a high amount of unknown degradation products, whose biocompatibility has then to be proven.

Therefore, the α-tocopherol has to be added to the finished product after crosslinking and annealing is applied. In this study, two methods are presented to incorporate α-tocopherol into crosslinked UHMW-PE: In the first method, simple sorption and diffusion in combination with annealing is used to add α-tocopherol to crosslinked UHMW-PE.

The second method uses supercritical CO_2 to incorporate α-tocopherol into the PE. Supercritical CO_2 is known for its high diffusion coefficient in polymers and is technically widely used for extraction of organic substances. It is non-toxic, inflammable and cheap. The solubility of α-tocopherol in supercritical CO_2 is governed by the equation [38]:

$$c = d^{8.231} \cdot e^{\frac{-17353.5}{T}} + 0.646$$

where c represents the α-tocopherol concentration in supercritical CO_2 [g/l], d the density of CO_2 [g/l] and T the temperature [K].

For both methods, the α-tocopherol-distribution and a possible oxidation of the UHMW-PE were determined with the help of a FTIR-microscope, a possible degradation of the α-tocopherol was investigated by means of high performance liquid chromatography (HPLC).

2 Materials and methods

2.1 Crosslinked UHMW-PE and α-tocopherol

Crosslinked UHMW-PE was Durasul® from Centerpulse Ltd. (Winterthur, Switzerland, now Zimmer, Inc.). This material is crosslinked by electron beam irradiation at a dose of 100 kGy and annealed under inert atmosphere for 2 h at temperatures above the melting point. The material was not sterilised with ethylene oxide. For the tests, $20 \times 20 \times 20\,mm^3$ cubes of crosslinked UHMW-PE were used. After the experiments with cubes, stabilisation was applied to finished hip cups from Zimmer, Inc.

DL-α-tocopherol (LOT-No.: UT02040015) was a gift sample of Hoffmann-La Roche (Grenzach-Wyhlen, Germany).

2.2 Sorption and diffusion in an autoclave vessel (method 1)

The UHMW-PE cube was fixed with a small screw with a shim onto a lead plate. This ensured that the cube did not swim and the α-tocopherol could diffuse into the cube evenly from all sides. The cube was put into an autoclave vessel "20S" from Roth (Karlsruhe, Germany), which was filled with pure α-tocopherol. Then, the vessel was purged with nitrogen for 10 min. After this purging, the valves were closed and the nitrogen pressure in the vessel was set to approx. 15 bar. A variation of this pressure had no measurable impact on diffusion. Afterwards, the vessel was heated up to the desired temperature, which was then kept constant for the duration of the experiment. Finally, the vessel was cooled down and the cube was taken out.

For a further homogenisation of the α-tocopherol distribution, the cubes were put in round-bottom flasks purged with nitrogen and stored in an oven at temperatures from 160°C to 200°C for several hours.

2.3 Diffusion with supercritical CO_2 (method 2)

For the impregnation of the UHMW-PE cubes a supercritical fluid apparatus was used (Speed SFE2, Applied Separations), as shown in Fig. 1.

The cube was placed in the high pressure cell by an inlet so that the cube was situated in the middle of the cell height. At the bottom of the cell, a certain mass of α-tocopherol

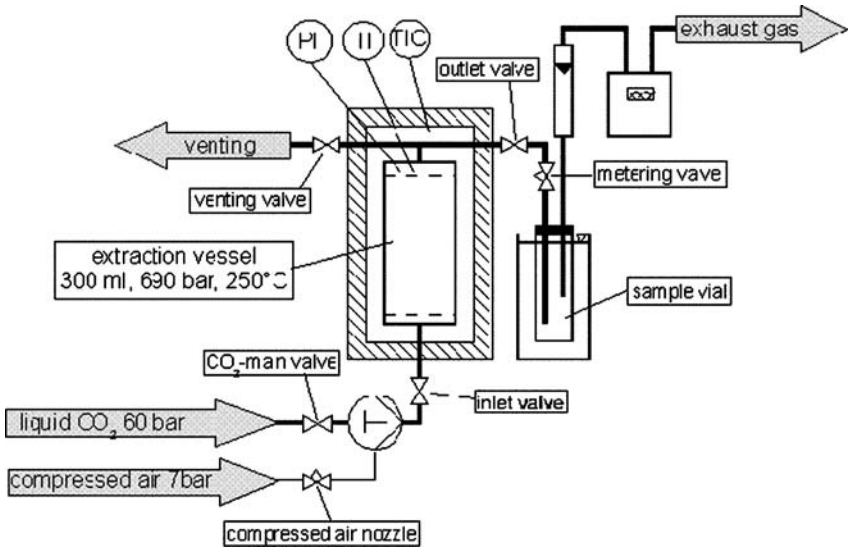

Fig. 1 Flow sheet of the high pressure apparatus.

was placed, depending on the desired final mass fraction of α-tocopherol in the product. After closing the high pressure cell it was flashed by CO_2 to remove all the air and oxygen, to prevent oxidation processes during the impregnation. After heating to the desired temperature (140–170°C) the pressure was adjusted (100–300 bar) by adding supercritical CO_2 with the air driven high pressure pump. At supercritical conditions the added amount of α-tocopherol is completely solved in the supercritical CO_2 and therefore impregnation takes place because of the excellent diffusion properties of the supercritical fluid. Following the impregnation step, pressure has to be released very slowly. If the pressure is decreased too fast, the CO_2 cannot diffuse from the UHMW-PE cube as fast as the surrounding pressure decreases, resulting in an overpressure inside the UHMW-PE cube. By this the structure of the polymer is destroyed resulting in cracks of the UHMW-PE cube, as shown in Fig. 2.

For optimisation of the impregnation by supercritical CO_2 different procedures were tested. The heating of the cell was tested at atmospheric conditions and under pressure (100–300 bar). For the depressurisation step releasing the pressure at impregnation temperature (140–170°C) was tested as well as cooling the cell to 40–80°C before decreasing pressure. To prevent cracking of the UHMW-PE cube also different velocities of releasing the CO_2 from the high pressure cell were tested.

2.4 FTIR measurements

After the experiments the cubes were sawed into two pieces. Thin films (approx. 150 μm) were cut off from the cut surface

Fig. 2 Picture of a UHMW-PE cube after too fast depressurisation.

with the help of a microtome cutter. Linescans were carried out across the middle of the films from one edge to the other with a Perkin Elmer® AutoImage FTIR-microscope connected to a Perkin Elmer® Spectrum One (aperture size: $100 \times 100\,\mu m^2$, resolution in wave number: $1\,cm^{-1}$, 16 scans per point, distance between points: $300\,\mu m$). 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 $2020\,cm^{-1}$.

The hip cups were also sawed in the middle into two equal pieces and thin films (approx. $150\,\mu m$) were cut off from the cut surface with the help of a microtome cutter. These films were fixed in the FTIR-microscope and mapscans were carried out over the whole area (aperture size: $100 \times 100\,\mu m^2$, resolution in wave number: $1\,cm^{-1}$, 16 scans per point, grid distance between points: $200 \times 200\,\mu m^2$). The α-tocopherol concentration was determined in the same way as described above.

The degree of oxidation of the UHMW-PE films was investigated by measuring the carbonyl number (CO-number) of the films (according to DIN 53383). The ratio of the peak area of the carbonyl peak at $1718 \pm 15\,cm^{-1}$ to the peak area of the UHMW-PE-peak at $2020 \pm 20\,cm^{-1}$ was evaluated as a direct measure for oxidative degradation.

All spectra were collected in transmission.

2.5 HPLC measurements

Analytical HPLC was performed at room temperature with a flow rate of 0.5 ml/min using a normal-phase silicagel column ($13\,\mu m$, Glass Works Kavalier, Votice, Czech Republic). The wavelength of the UV/V is detector (UV/VIS Detector Merk Hitachi L7450A, Hitachi, Tokyo, Japan) was set to 295 nm, the eluent was *n*-heptane/*i*-propanol 995/5 v/v.

The cubes were cut in films (approx. $300\,\mu m$) to enlarge the surface for faster extraction. Approx. 0.5 g of the films were put in 100 ml *n*-heptane/*i*-propanol 995/5 v/v in an autoclave vessel and purged with nitrogen for 15 min. The α-tocopherol and its possible degradation products were extracted at 185°C for 3.5 h. 1000 μl of the extract were injected in the HPLC.

The mass fraction of degradation products was calculated by comparing the area of the α-tocopherol-peak to the sum of the area of the peaks of the degradation products.

3 Results

3.1 Method 1: Simple sorption and diffusion

In the first experiments, the temperature was set to 100°C and the diffusion time was varied from 24 to 96 h. At this temperature, the heat distortion of UHMW-PE is negligible. As can be seen in Fig. 3, the edge concentration is the same for all samples, but the penetration depth increases with rising duration of diffusion. Although it is not possible to realise high penetration depths with this method within a reasonable time, it still enables the sensitive edge layers of finished products to be stabilized with a varying α-tocopherol concentration ensuring superficial protection from oxidative degradation.

In order to achieve a higher diffusion rate, the temperature was raised. The diffusion coefficient increases especially when exceeding the melting point, since cristalline layers can be considered as diffusion barriers [39, 40]. But besides the diffusion coefficient, the solubility of α-tocopherol also increases with rising temperature (compare Figs. 3–6). Figure 4 shows the linescan of a cube, which was in the autoclave for 2 h at 130°C resulting in an edge concentration

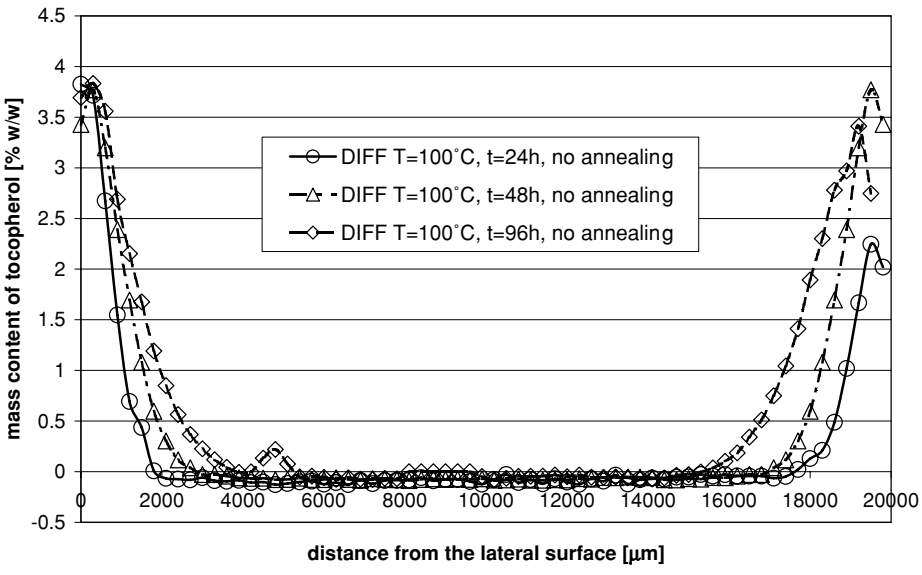

Fig. 3 Conventional diffusion of α-tocopherol at 100°C for varying periods of time. Longer diffusion leads to a higher penetration depth with comparable edge concentrations.

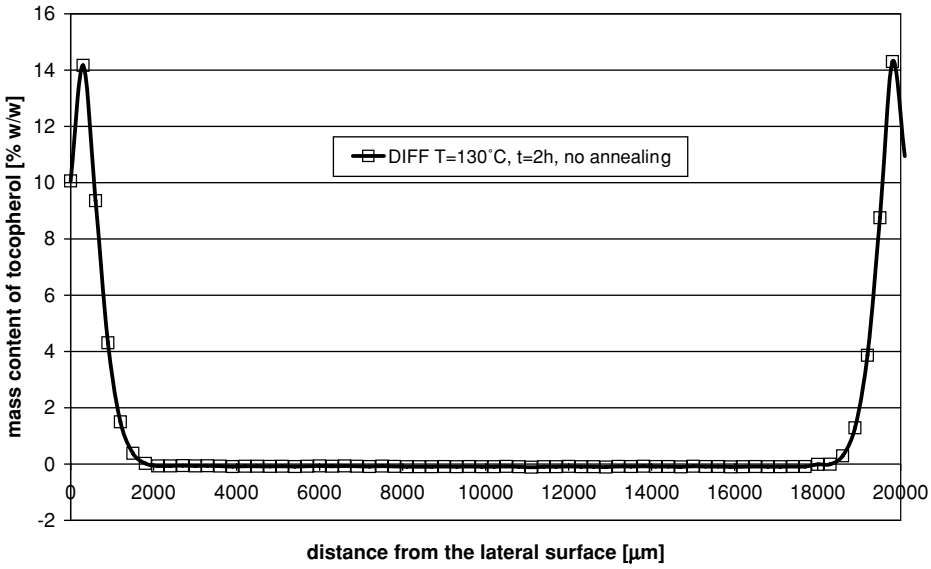

Fig. 4 α-Tocopherol distribution after diffusion at 130°C for 2 h (no annealing).

of approx. 14% w/w. At 200°C, 40% w/w α-tocopherol may be incorporated in crosslinked UHMW-PE, a huge amount considering that 0.4% w/w represent a sufficient stabilisation in most cases. Obviously, this amount is far beyond the saturation concentration of α-tocopherol in crosslinked UHMW-PE at room temperature resulting in a heavy bleeding of the cubes after the experiments. Furthermore, concentrations beyond 2% of α-tocopherol act as plasticizer for UHMW-PE.

A comparison of all results shows that the diffusion temperature influences the penetration depth as well as the edge concentration (sorption), whereas the diffusion time only influences the penetration depth.

Raising the temperature to realise faster diffusion leads to too high edge concentrations of α-tocopherol, as described above. One possibility to prevent this would be to dilute the α-tocopherol with a suitable solvent, but with respect of an application *in vivo*, the introduction of a further component, whose biocompatibility for clinical admittance probably has to be proven, should be scrutinized critically.

To achieve a more homogeneous α-tocopherol distribution, the cubes were annealed in nitrogen for several hours at elevated temperatures in round-bottom flasks. The α-tocopherol from the edge layers diffuses in the middle of the cube resulting in a more homogeneous distribution (approx. 20% also blooms out during 24 h of annealing at 160°C). Figs. 5 and 6 show homogenisation through annealing at different temperatures and for varying periods of time. The cube in Fig. 6 was in the autoclave for 1 h at 130°C. Annealing at 200°C for 24 h leads to an almost homogeneous distribution of approx. 0.4%. In Fig. 5, the cube was stored in α-tocopherol in the autoclave at 130°C for 2 h. Annealing at 200°C for 22 h leads to a nearly homogeneous concentration throughout the cube of approx. 1% α-tocopherol.

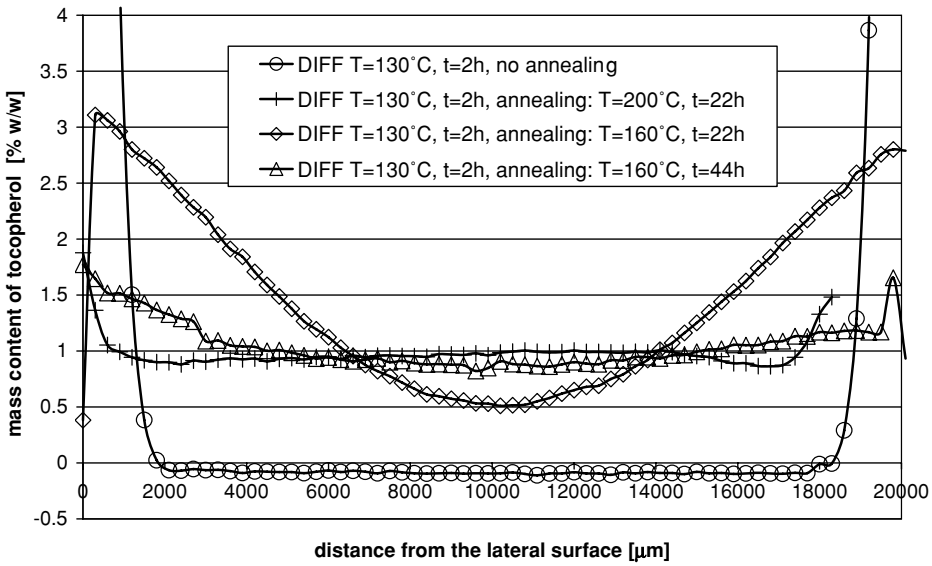

Fig. 5 Homogenisation of the high edge concentration of α-tocopherol after diffusion through annealing in inert atmosphere.

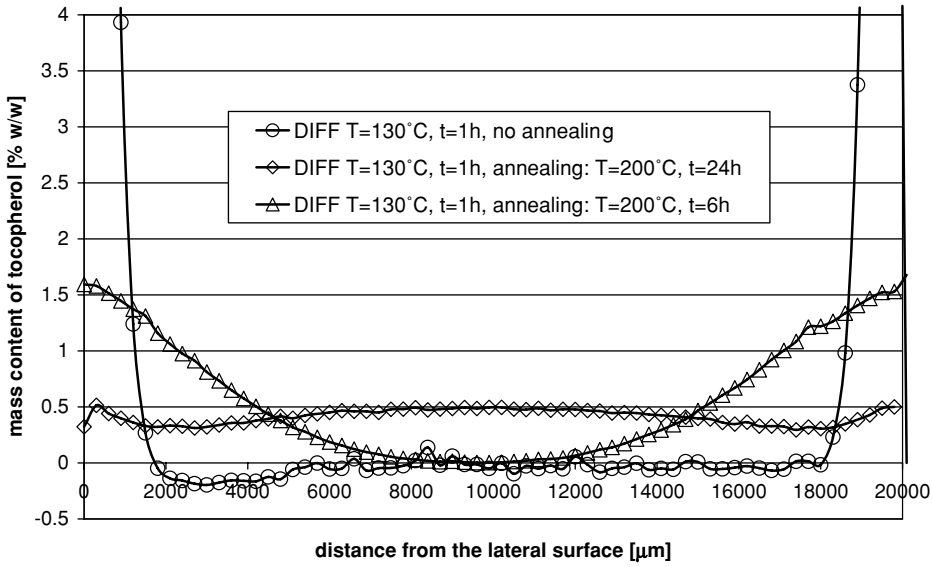

Fig. 6 A nearly homogeneous α-tocopherol distribution of approx. 0.4% w/w can be realised by diffusion at 130°C for 1 h and subsequent annealing at 200°C for 24 h.

The duration and temperature of the diffusion in the autoclave determine the overall content of α-tocopherol in the cubes, the duration and temperature during the annealing process the local distribution of α-tocopherol. A stabilisation of the sensitive edge layer as well as a nearly homogenous distribution with varying α-tocopherol content may be realised by varying the process parameters. Concerning the stabilisation of articulating surfaces of endoprostheses, it may be questioned whether a homogeneous distribution of α-tocopherol throughout e.g. a hip-cup really is necessary. It may be sufficient to stabilise the sensible edge layers resulting in a much shorter and gentler processing. Annealing at 200 °C for 6 h results in a penetration depth of approx. 8 mm.

Strict exclusion of oxygen during diffusion and annealing does not cause any oxidative degradation of the UHMW-PE, as can be seen in Fig. 7.

The HPLC-analysis of the cube showed a degradation of α-tocopherol of 11%. Adding the α-tocopherol to the UHMW-PE powder before processing as it is applied to conventional UHMW-PE, leads to a degradation of approx. 30%.

3.2 Method 2: diffusion with supercritical CO_2

Similar to the experiments with sorption and diffusion, the diffusion coefficient is mainly influenced by the temperature and the duration of the process. Raising the temperature results in an increase of diffusion speed, especially when the melting point is exceeded, as can be seen in Fig. 8. Longer diffusion time leads to a higher penetration depth (see Fig. 9).

Changing the CO_2-pressure has a big impact on the amount of α-tocopherol diffusing into the UHMW-PE. The solubility of α-tocopherol in CO_2 (see formula in the

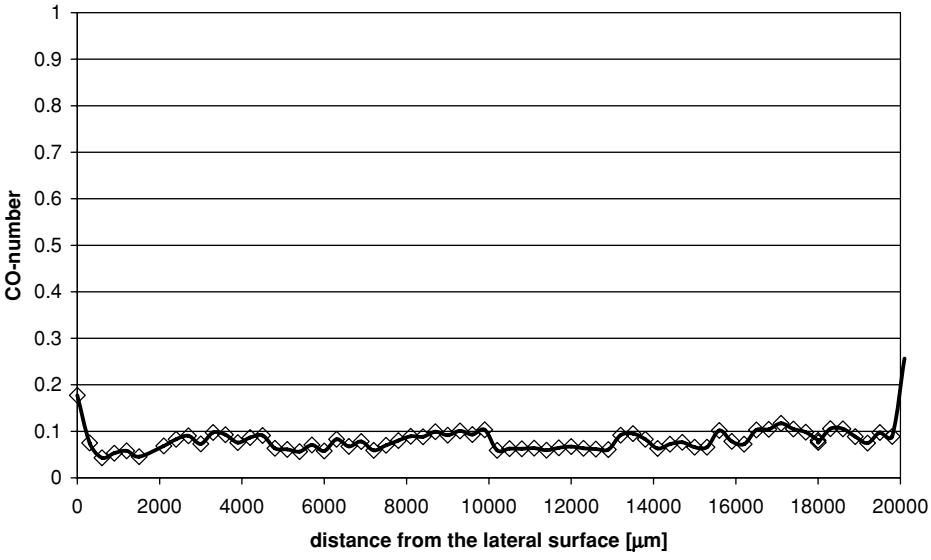

Fig. 7 Oxidation index (CO-number) of a cube after annealing for 6 h at 200°C.

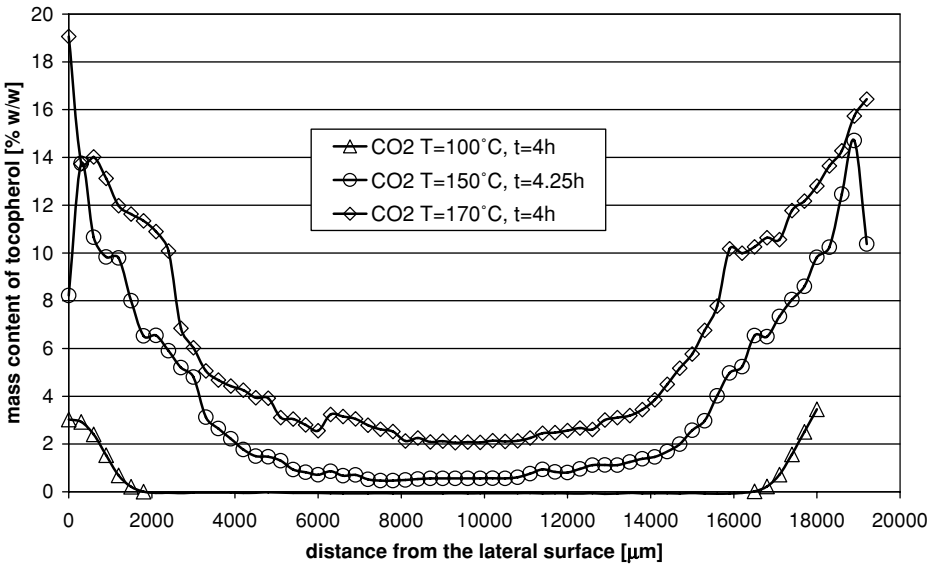

Fig. 8 Impact of the temperature on the diffusion of α-tocopherol with supercritical CO_2.

introduction) as well as the diffusion rate of CO_2 depends on the CO_2-density and thus on the pressure. Decreasing the pressure from 300 bar to 150 bar resulted in a noticeable lower α-tocopherol-content, as can be seen in Fig. 10. The pressure was set to 300 bar for all experiments.

A great advantage of the impregnation with supercritical CO_2 compared to conventional diffusion is that the maximum concentration of α-tocopherol in the UHMW-PE can be set by the concentration of α-tocopherol in CO_2. Figure 11 shows experiments with different α-tocopherol-concentrations in the CO_2. Decreasing the concentration leads to a lower mean mass fraction of α-tocopherol in the UHMW-PE.

A stabilisation of the sensitive edge layer as well as a nearly homogenous distribution with varying α-tocopherol content may be realised by varying the process parameters as well as by varying the starting concentration of α-tocopherol in the CO_2. No oxidation of the UHMW-PE could be detected in the specimens.

In the HPLC analysis, only a very low amount of degradation products of α-tocopherol (6–10%) could be detected.

After the successful experiments with cubes, hip cups were stabilised with α-tocopherol using supercritical CO_2. Figure 12 shows the mapscan of a hip cup, which was impregnated at 170°C for 12 h at 300 bar resulting in a nearly homogeneous distribution of approx. 1% w/w α-tocopherol throughout the cup. The distortion of the stabilised cup was very small, in the magnitude of the increase in volume due to the stabilizer addition.

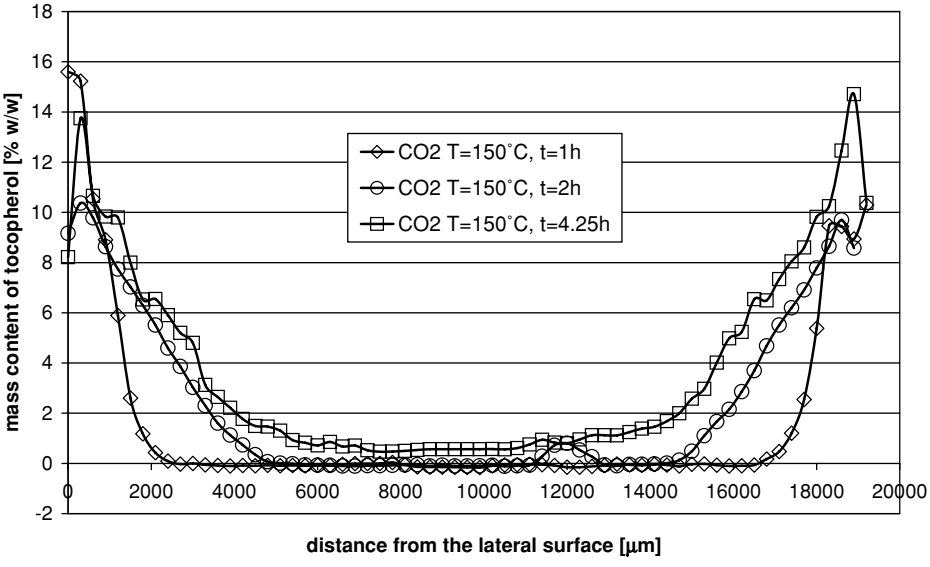

Fig. 9 Diffusion of α-tocopherol with supercritical CO_2 at 150°C for varying periods of time. Longer diffusion leads to a higher penetration depth with similar edge concentrations.

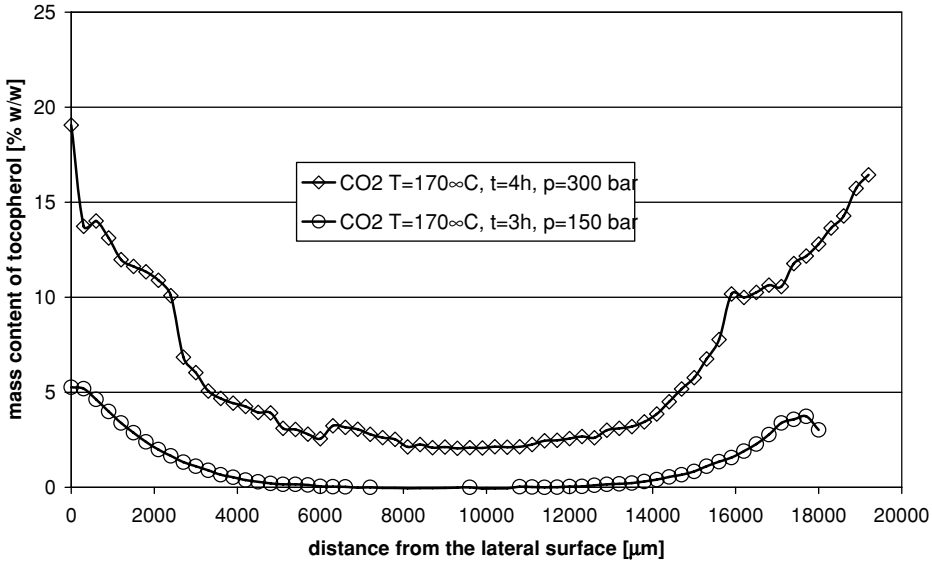

Fig. 10 The impact of the CO_2-pressure during diffusion on the α-tocopherol -distribution.

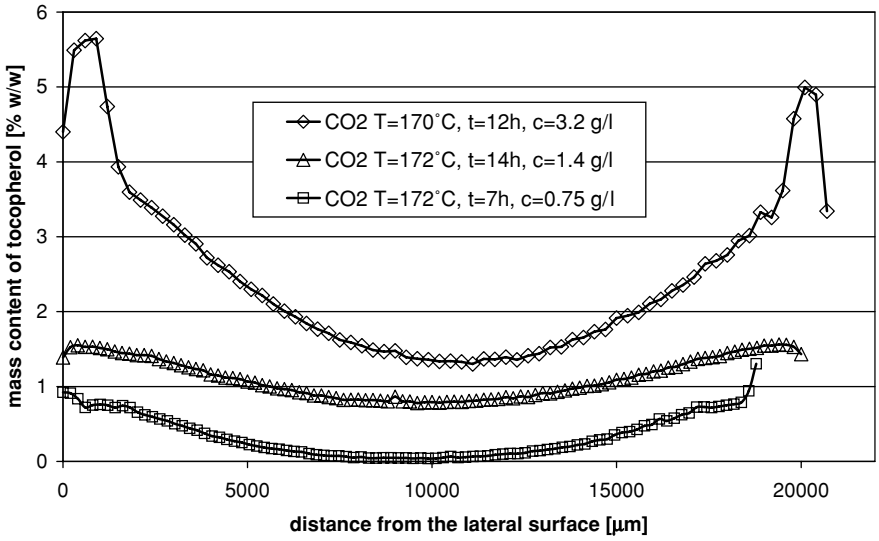

Fig. 11 The influence of the α-tocopherol concentration in the supercritical CO_2 on the amount of α-tocopherol in the UHMW-PE after diffusion.

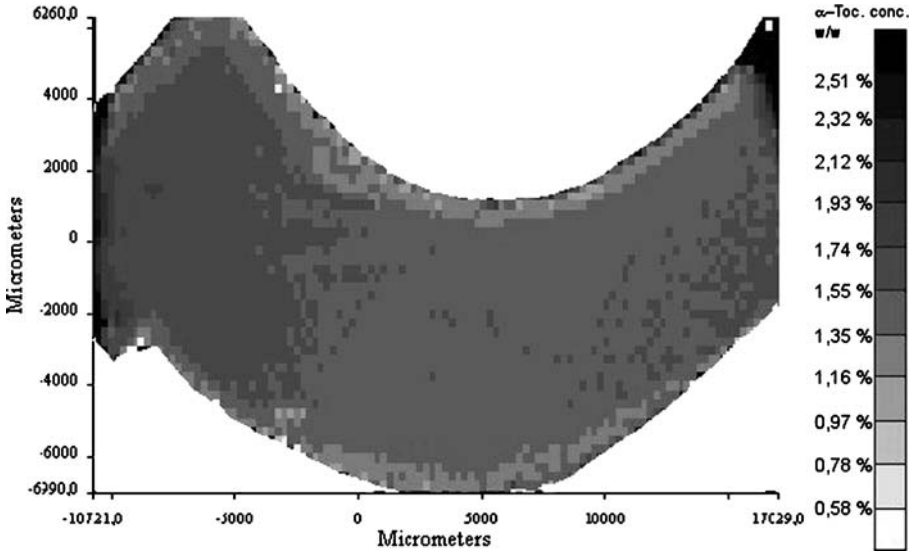

Fig. 12 α-Tocopherol distribution in a hip cup after impregnation with supercritical CO_2.

Conclusions

Both methods presented are very well suited to stabilise crosslinked UHMW-PE with α-tocopherol. A stabilisation of the sensitive edge layer as well as a nearly homogenous distribution with varying α-tocopherol content may be realised by varying the process parameters. Method 2 with supercritical CO_2 has the advantage that the amount of α-tocopherol diffusing into the UHMW-PE can be set easier and that the process temperatures are lower (170°C compared to 200°C) resulting in less stress for the material.

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

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