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SCIENTIFIC PAPER

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SUPERCRITICAL CO_2 IMPREGNATION OF POLYETHYLENE COMPONENTS FOR MEDICAL PURPOSES*

Modern hip and knee endoprosthesis are produced in titanium and to reduce the friction at the contact area polymer parts, mainly ultra–high molecular weight polyethylene (UHMW–PE), are installed. The polyethylene is impregnated with α–tocopherol (vitamin E) before processing for remarkable decrease of oxidative degradation. Cross linked UHMW–PE offers much higher stability, but α–tocopherol cannot be added before processing, because α–tocopherol hinders the cross linking process accompanied by a heavy degradation of the vitamin. The impregnation of UHMW–PE with α–tocopherol has to be performed after the cross linking process and an accurate concentration has to be achieved over the cross section of the whole material.

In the first tests UHMW–PE–cubes were stored in pure α–tocopherol under inert atmosphere at temperatures from 100 to 150 °C resulting in a high mass fraction of α–tocopherol in the edge zones and no constant concentration over the cross section.

For better distribution and for regulating the mass fraction of α–tocopherol in the cross linked UHMW–PE material supercritical CO_2 impregnation tests were investigated. Again UHMW–PE–cubes were impregnated in an autoclave with α–tocopherol dissolved in supercritical CO_2 at different pressures and temperatures with variable impregnation times and vitamin E concentrations.

Based on the excellent results of supercritical CO_2 impregnation standard hip and knee cups were stabilized nearly homogeneously with varying mass fraction of α–tocopherol.

Approx. 70% of all hip– and knee–endoprostheses world–wide are equipped with articulating surfaces made of ultra–high molecular weight polyethylene (UHMW–PE), see Figure 1. 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 [1–9]. This degradation can be delayed remarkably by adding the natural antioxidant α–tocopherol (vitamin E) to the UHMW–PE. The biocompatibility tests of this new compound are at an advanced stage and clinical studies are in preparation.

More and more importance gains cross linked UHMW–PE (CL–UHMW–PE), a consequential further development of conventional UHMW–PE. This CL–UHMW–PE is cross linked by electron beam irradiation and annealed subsequently. The network structure produced by this treatment leads to an improved wear resistance. Especially hip simulator tests proved the cross linked material to possess a considerable higher wear resistance than standard UHMW–PE.

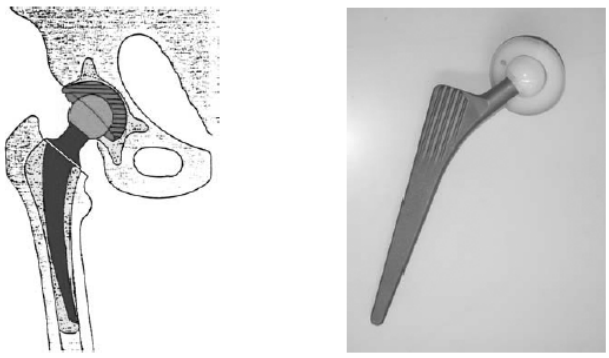

Figure 1. Hip endoprostheses

For the conventional UHMW–PE the α–tocopherol is added to the polymer before processing, which is not possible for CL–UHMW–PE, because α–tocopherol acts as a radical scavenger, hindering the cross linking 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 cross linking 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 cross linking and annealing is applied.

*Rad saopšten na VII simpozijumu "Savremene tehnologije i privredni razvoj", Leskovac, 19. i 20. oktobar 2007. godine

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Paper received: Jun 07, 2007
Paper accepted: July 05, 2007

For this reason the impregnation of the finished product by supercritical CO_2 was tested. 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 calculated by the Chrastil equation [10]:

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

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]. The parameters for the Chrastil equation were fitted from literature data [11,12].

The α–tocopherol–distribution and a possible oxidation of the CL–UHMW–PE were determined with the help of a FTIR–microscope and a possible degradation of the α–tocopherol was investigated by means of high performance liquid chromatography (HPLC).

EXPERIMENTAL PART

For the tests, 20x20x20 mm^3 cubes of CL–UHMW–PE (cross linked UHMW–PE) were used. The CL–UHMW–PE was Durasul® from Centerpulse Ltd. (Winterthur, Switzerland, now Zimmer, Inc.). After the successful experiments with the cubes the finished hip cups from Zimmer, Inc. were also impregnated.

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

A supercritical fluid apparatus (Speed SFE2, Applied Separations) was used for the impregnation tests of the cubes. The cube was placed in the middle of the cell height by an inlet. At the bottom a calculated mass of α–tocopherol was placed, depending on the desired final mass fraction of α–tocopherol in the product. To prevent oxidation processes during the impregnation the high pressure cell was flashed by CO_2 to remove all the air and oxygen. 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 these supercritical conditions the added amount of α–tocopherol is completely dissolved in the supercritical CO_2 and therefore impregnation takes place because of the excellent diffusion properties of the supercritical fluid. After the impregnation step the pressure has to be released very carefully. Too fast depressurisation results in a destruction of the CL–UHMW–PE cube.

Different procedures for impregnation were tested. The cell was heated as well at atmospheric conditions as under pressure (100 – 300 bar). Depressurisation was tested at impregnation temperatures (140 – 170 °C) and also after cooling to 40 – 80 °C. Also different depressurisation velocities were tested to prevent cracking of the cubes.

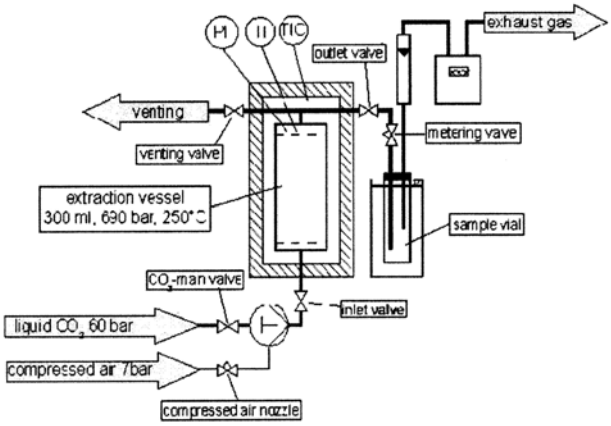

Figure 2. Supercritical fluid apparatus

RESULTS AND DISCUSION

Based on temperature dependency of the diffusion coefficient a temperature increase raises the speed of diffusion, especially when the melting point of the polymer is exceeded (140 °C). As shown in Figure 3 only at temperatures above the melting point sufficient impregnation was achieved at impregnation times of 4 hours.

An increase of impregnation time leads to higher penetration depth up to a constant concentration of α–tocopherol over the whole volume of the cube.

Based on the solubility behaviour of substances in supercritical fluids an increase in pressure results in higher solubility of α–tocopherol in the supercritical CO_2 and thus in higher concentration in the UHMW–PE cube, as shown in Figure 3.

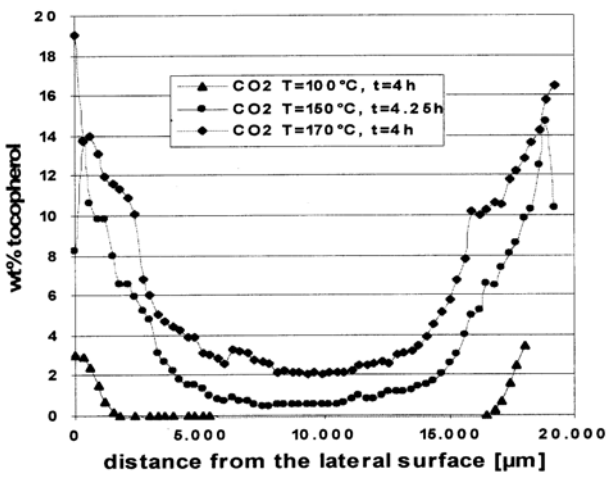

Figure 3. Influence of temperature on α–tocopherol concentration (wt%) in CL–UHMW–PE

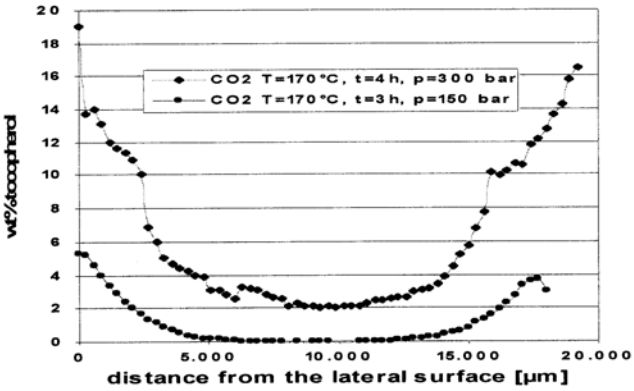

Figure 4. Influence of pressure on α–tocopherol concentration (in wt%) in CL–UHMW–PE

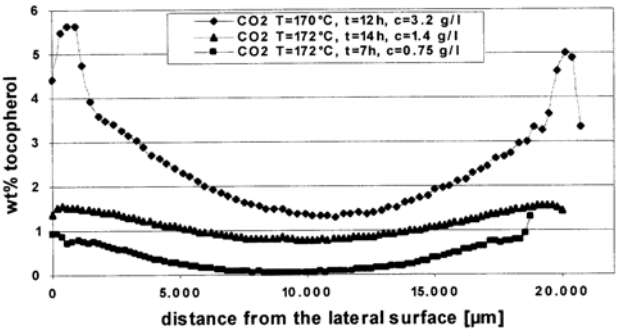

Figure 5. Influence of different α–tocopherol concentration (in wt%) in CL–UHMW–PE

The great advantage of this impregnation method is that the concentration of α–tocopherol in the UHMW–PE cube can be adjusted to desired levels by changing the amount of α–tocopherol in the impregnation cell (see Figure 5). The higher concentrations at the surfaces of the cubes result from different effects. On one side the whole process is diffusion controlled, resulting in this typically concentration profile. On the other side during the depressurisation step CO_2 density is lowered and thus α–tocopherol falls out from the one phase mixture and covers the surface of the cubes. The last but not the least, during the depressurisation step CO_2 diffuses from the centre to the surface, causing an enrichment of α–tocopherol at the surface. For industrial impregnation process this arises no problems, because after impregnation the polymer parts will be adjusted for each prosthesis individually and so the surface with the high concentration will be removed.

After the successful experiments with cubes real hip cups were impregnated with α–tocopherol using supercritical CO_2. The mapscan of a hip cup is shown in Figure 6, which was impregnated for 12 hours at 170 °C and 300 bar, resulting in a nearly homogeneous distribution of approx. 1 wt% α–tocopherol over the cross section in the whole cup.

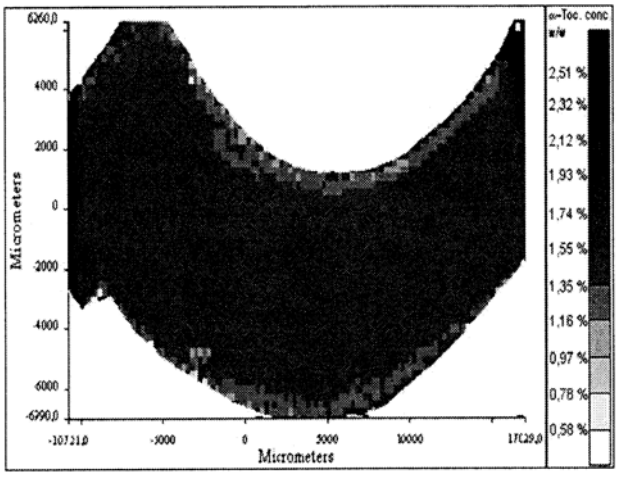

Figure 6. α–tocopherol concentration (in wt%) in real hip cups

CONCLUSIONS

The supercritical CO_2 impregnation of CL–UHMW–PE (crosslinked UHMW–PE) with α–tocopherol could be performed successfully. 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.

Based on the excellent results of supercritical CO_2 impregnation standard hip and knee cups were stabilized nearly homogeneously with varying mass fraction of α–tocopherol. A pilot plant for realisation of CO_2 impregnation of standard hip and knee cups for prosthesis is already in construction, where up to 30 prosthesis can be impregnated per batch. Parallel further optimisation, especially of the depressurisation step, will be done to reduce the total treatment time per batch.

ACKNOWLEDGEMENTS

We like to thank DI W. Schneider and Dr. M. Schneider 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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IZVOD

IMPREGNACIJA POLIETILENSKIH KOMPONETI ZA MEDICINSKE NAMENE NADKRITIČNIM CO_2

(Naučni rad)

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Savremene endoproteze kukova i kolena proizvode se od titana, a da bi se smanjilo trenje kontaktnih površina ugrađuju se polimerni delovi, i to uglavnom od polietilena velike molekulske težine (UHMW–PE). Pre obrade, polietilen se impregniše sa α–tokoferolom (vitamin E) koji značajno smanjuje degradaciju oksidacijom. Poprečno vezivanje UHMW–PE omogućava veću stabilnost, ali se α–tokoferol ne može dodavati pre obrade, zato što α–tokoferol sprečava procese poprečnog vezivanja, praćene izraženom degradacijom vitamina. Impregnacija UHMW–PE sa α–tokoferol mora se izvesti posle procesa poprečnog vezivanja i tačna koncentracija mora se postići duž celokupnog poprečnog preseka materijala.
U prvim ispitivanjima, UHMW–PE kocke su držane u čistom α–tokoferolu u inertnoj atmosferi na temperati od 100 do 150 °C, što je rezultiralo u velikom masenom udelu α–tokoferola u ivičnim zonama i promenljivoj koncentraciji duž poprečnih preseka. U cilju bolje raspodele kao i regulacije masenog udela α–tokoferola u poprečnim vezivanju UHMW–PE materijala, ispitivana je nadkritična CO_2 impregnacija. Ponovo, UHMW–PE kocke su impregnisane u autoklavu sa α–tokoferolom rastvorenim u nadkritičnom CO_2 na različitim pritiscima i temperaturama sa različitim vremenima impregnacije i koncentracijama vitamina E.
Na osnovu odličnih rezultata impregnacijom nadkritičnim CO_2, čašice veštačkih kukova i kolena su približno homogeno stabilisane sa različitim masenim udelima α–tokoferola.

Ključne reči: Nadkritični CO_2 • Impregnacija • Polimer • Endoproteza •

Key words: Supercritical CO_2 • Impregnation • Polymer • Endoprostheses •