

# SUPERCRITICAL CO<sub>2</sub> IMPREGNATION

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## INTRODUCTION

Apart from high pressure extraction supercritical CO<sub>2</sub> impregnation has been a major topic in high pressure process development during the last 20 years. Research covers a wide range of applications for high value products, which are processed in small plants, e.g. impregnation of cross-linked UHMW-PE with  $\alpha$ -tocopherol for medical purposes, which can be used for endoprostheses. On the other hand low price products like spruce wood are impregnated in large plants. Medium sized plants are used e.g. for the impregnation of metal complexes into polymer fibers, followed by electroless plating. Further the impregnation of cellulose fibers with  $\alpha$ -tocopherol and D-panthenol was investigated for special medical skin protection purposes or for the production of cellulose towels with disinfection effect. In the food industry the most promising process is the impregnation of nuts with antioxidants. Every year thousands of tons of nuts cannot be used in the food industry because of rancidity.

## IMPREGNATION OF WOOD

Timber is a very important constructional material for indoor and outdoor purposes.

Very often it is exposed to environmental impacts like water, wind, sunlight or even biological attacks like insects, rot or fungus. Such attacks cause big damages and result in costly renovation requirements comparable to corrosion problems with iron constructions [3].

In order to prevent such damages surfaces are sealed and/or biocides are deposited in the wood. Surface sealing is typically done by painting with substances containing biocides, UV blockers and materials which prevent moisture penetration. The treatment with biocides is normally done by depositing the active ingredients in the wood by vacuum or pressure.

Larger structural timber or wood mainly for outdoor uses like poles or garden fences are pressure impregnated with different metal salts.

Smaller structural wood mainly for doors and windows is mainly impregnated with different biocides solved in organic solvents using the vacuum method.

Impregnation of wood with the help of supercritical carbon dioxide has been investigated during the last two decades [1, 2]. Very early it was detected that supercritical carbon dioxide penetrates completely through the wood together with the solved biocides. But there is a gradient in concentration of biocides depending on thermodynamic conditions and the kind of wood. It seems that it is not the result of incomplete penetration of the wood by the supercritical CO<sub>2</sub>/biocides mixture. This gradient can be caused by different adsorption and desorption processes, by re-extraction of biocides from the wood during depressurization or

the biocides get filtered from the carbon dioxide as the solution fills up the wood matrix. Understanding of biocides deposition in the wood matrix is an important part of the continuous development of the supercritical wood impregnation process, especially for larger dimensions. The latest results by A.W. Kjellow and O. Henriksen [2] show, that the biocides separate chromatographically from the CO<sub>2</sub> during pressurization. On the other hand there is a flow of CO<sub>2</sub> out of the wood and part of the biocides leave the wood during depressurization. Normally there is a high wood affinity of the biocides that helps that the biocides remain in the wood.

Another main research topic is minimizing the treatment time in order to increase the economic viability of the supercritical treatment process. A lot of research was done to examine the effect of different pressurization and depressurization rates on the mechanical properties of the impregnated wood. The latest results show that the pressurization rate is not the limiting factor but the velocity how fast the biocides can be delivered to the centre of the impregnated samples. This means that the biocides have to be moved as fast as possible through the wood structure. This includes an increasing gas phase concentration of biocides during pressurization and if necessary addition of a co-solvent to the CO<sub>2</sub>. During pressurization the pores are filled up with the biocide mixture and the biocides are separated chromatographically from the CO<sub>2</sub>, which causes a concentration gradient from the surface of the wood towards to the centre. When the impregnation pressure is reached there is no further CO<sub>2</sub> flow into the wood and the concentration differences must be equalized by diffusion, which needs a certain time depending on the size of the wood. During depressurisation there is a CO<sub>2</sub> flow out of the wood, but due to the high wood affinity of the biocides to the wood, most of them are kept in the wood. There are also big differences between the different kinds of wood, especially regarding diffusion velocity. Pine wood is generally considered to have a better permeability than fir and spruce wood and during impregnation damage occurs seldom in pine wood compared to fir and spruce wood.

The most important active ingredients for wood impregnation are tebuconazole and probikonazole which have been successfully used for vacuum impregnation since the early 1990`s. Although comprehensive knowledge was not yet available the company Supertrae A/S in Hampen, Denmark started commercial wood impregnation by means of supercritical CO<sub>2</sub> in 2002 as shown in Figure 2. They started directly with an industrial size plant which caused some problems at the beginning. But this investment induced strong development efforts in the wood industry.

The deposition of tebuconazole is optimal in the pressure range from 120 bar to 250 bar. The biocide retention increases when the pressure is raised up to 250 bar. This can be mainly explained by the increased solvent power of supercritical fluids at higher pressures. A further pressure increase above 300 bar decreases the biocide retention. Perhaps the solubility of the biocide is then so high, that the deposition of the substance in the wood is reduced. Especially at pressures of 120 bar to 150 bar the equilibrium of biocide in wood to biocide in CO<sub>2</sub> is moved towards to the wood and insures an optimal deposition of the biocide.

### **The process**

The actual impregnation process can be described as follows: Figure 1

- The wood is placed in the impregnation vessel
- The required amount of active ingredients is placed in a mixing vessel

- CO<sub>2</sub> flows into the cycle, pressure and temperature are adjusted to the desired impregnation conditions, whereby the active ingredients are dissolved in the CO<sub>2</sub>
- CO<sub>2</sub> together with the active ingredient is circulated through the impregnation vessel for a certain time to ensure an even distribution of the active ingredients in the wood
- The vessel is depressurized and any excess active ingredients are separated in a separation vessel, so that the CO<sub>2</sub> and the active ingredients can be recycled

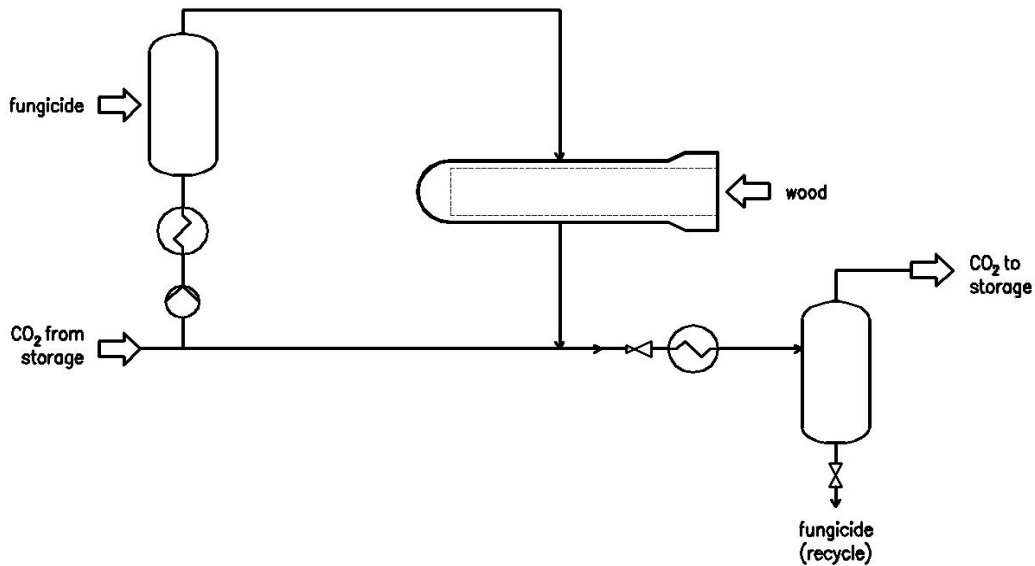


Figure 1. Flow sheet of an impregnation plant

As the solubility of water in CO<sub>2</sub> is quite low at usual impregnation conditions, the moisture of the wood is only minimally changed during the process.

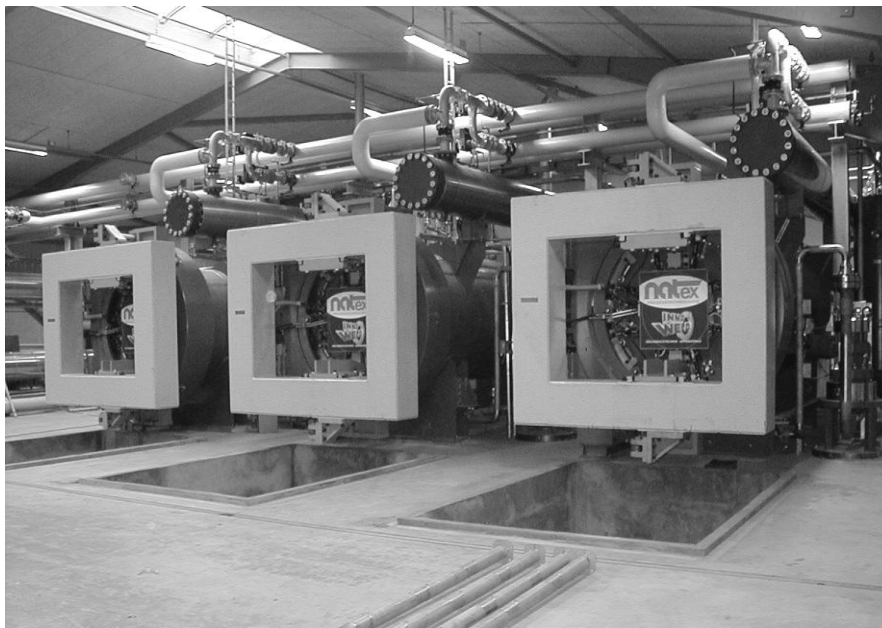


Figure 2. Impregnation plant (courtesy of Superwood)

## **Properties of impregnated wood after the Superwood™ process**

Numerous examinations have been carried out, which document that the process does not affect the mechanical characteristics of wood and does not change the moisture content.

As the product is not very long on the market, the experience with the durability is still limited. Tests in Denmark and in Malaysia show that the provided protection is equal or better than the protection of products treated with competing processes.

Wood impregnation is not only limited to avoidance of fungi and bacteria attack, but can also be used to increase fire resistance, to increase water resistance, to dye the wood especially for furniture and floors and to harden the wood surface.

## **IMPREGNATION OF OIL CONTAINING FRUITS AND SEEDS**

Most oil containing seeds contain monounsaturated or polyunsaturated fatty acids in the oil or fat. These essential fatty acids are the main reason why they are considered to be an important part of human nutrition. Oil containing seeds are e.g. soy beans, coconuts, peanuts, walnuts, hazelnuts, almonds, macadamia nuts, pumpkin seeds, rape seeds, sunflower seeds or wheat germs. Higher amounts of monounsaturated or polyunsaturated fatty acids increase the danger of oxidation of the oils, so that the oil fruits tend to get rancid. Rancid odors totally penetrate food and create enormous damages in the food industry. Until now nuts could only be protected from oxidation by coating them with an edible layer, which is impermeable by air. For these coatings usually combinations of whey proteins and sugar are used. After treatment the oil fruits have to be dried which causes further costs. The admixing of antioxidants to food only works with pasty or liquid products, e.g. hazelnut paste. The aim of recent development was to prolong shelf life of oil containing fruits and seeds without a dense coating and without the necessity to dry the products afterwards. The process developed by Adalbert-Raps-Stiftung uses the rapid diffusion of compressed gases into the oil containing fruits, which should be impregnated [4]. During the process of impregnation carnosol and/or carnosic acid are dissolved in the compressed gas and are transported into the matrix by the gas. Mainly CO<sub>2</sub> is used as compressed gas. The advantages of this gas are well known. The impregnation conditions are in the range of 50 to 350 bar and 40 to 70°C. Carnosol and carnosic acid are natural antioxidants, which are widely used in the food industry. Further carnosol and carnosic acid are very well distributed in the matrix of the oil containing fruit and consequently provide antioxidant activity in the whole fruit. Therefore chopped ground or whole fruits can be impregnated. The oil containing part of the fruit must not be covered by a diffusion inhibiting shell. The necessary concentrations of impregnating antioxidants are similar to those of conventional treatment. Antioxidants can be applied in different ways. It can be deposited on the surface of the oil fruits before the impregnation itself is started or it is dissolved in the CO<sub>2</sub> during pressurization in the impregnation vessel. The best results are achieved if carnosol and carnosic acid are mixed under pressure in a static mixer with the compressed gas and afterwards the mixture is expanded to atmospheric pressure. In this way a spray of fine droplets of the antioxidative solution is created and deposited on the oil fruits. The moistened oil fruits are afterwards treated with supercritical CO<sub>2</sub> in an impregnation vessel. During pressurization CO<sub>2</sub> penetrates into the fruits and transport the antioxidants into the matrix. The impregnation conditions are maintained for a certain time, so that equal

concentrations can be achieved by diffusion. After depressurization and emptying of the impregnation vessel drying of the fruits is not necessary.

Table 1 shows the extension of stability after supercritical impregnation with carnosol and carnosolic acid containing extract. The impregnation conditions were 300 bar and 60°C and the concentration of carnosic acid in the hazelnut was 50 ppm.

Storage [days]	peroxide number of the treated sample	peroxide number of the untreated sample
1	0	0
7	0	7
9	0	150
14	2	212

Table 1: Stability increase of hazelnut with supercritical impregnation

A further application is the stabilization of roasted coffee beans. On the one hand the shelf life of coffee beans can be extended with carnosic acid, on the other hand the beans can also be impregnated with certain aroma components, e.g. cinnamon, cardamom or vanilla.

## IMPREGNATION OF POWDERS FOR PHARMACEUTICAL PURPOSES

Because of the low solubility of most active pharmaceutical ingredients (APIs) in supercritical fluids only low to medium loadings in porous materials can be reached. For higher loadings an additional solvent must be added to the CO<sub>2</sub> as entrainer like CH<sub>2</sub>Cl<sub>2</sub>, DMSO and similar solvents [5]. On the other hand a lot of active ingredients are water soluble with a very poor solubility in CO<sub>2</sub> which makes them unsuitable for supercritical technology. For these ingredients only the antisolvent process can be of interest in the future.

For this purpose the porous material is soaked with an ethanol solution of the active ingredients and then put into the autoclave. During pressurization the ethanol is solved in the supercritical fluid and the active ingredients are precipitated on the porous material.

Supercritical fluid plants for the pharmaceutical industry will have to meet GMP requirements and FDA validations, which are difficult to be implemented for high pressure technologies. Further the validation of the cleaning procedures will be a future challenge for the pharmaceutical industry when using supercritical fluid technology at high pressures. One of the main targets in the future is the production of advanced products with controlled released properties.

## IMPREGNATION OF METAL COMPLEXES INTO POLYMERS

Apart from dyeing of textiles, which is widely published in the literature, the impregnation of functional substances into fibres and foils offers a wide field of new applications. CO<sub>2</sub> diffuses into the polymer, starts to swell the polymer and is able to carry the active substances far into the polymer. During the last years a lot of new ideas were tested using this phenomenon in order to produce new fibres and foils with functional surfaces. One of the first ideas was to impregnate surfaces so that non-conductive polymers are transformed into

conductive materials by electroless plating. The main goal was to reduce the demand for chemicals and the amount of wastewater as it was the case with supercritical dyeing. As a result of these development efforts a lot of new functional surfaces were created which could hardly be produced with conventional processes.

### Electroless plating of aramid fibres [6]:

As a first step the swelling polymer consisting mainly of aramid was impregnated with metal organic compounds. After the impregnation process a metal film was deposited on the polymer surface by conventional electroless plating as shown in Figure 3.

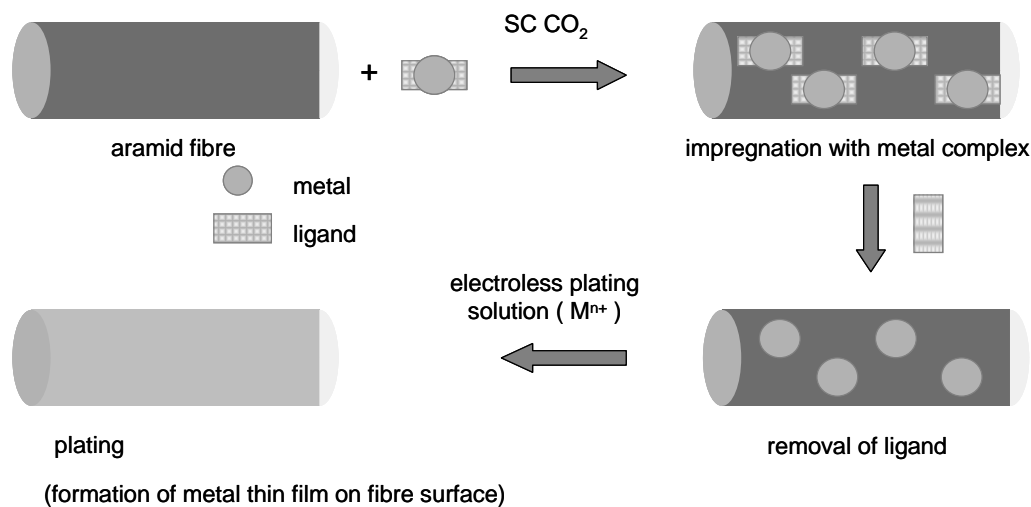


Figure 3. Production of conductive surfaces by impregnation with metal organic substances.

Different Kevlar® fibres like DTX1670, T732 or T740 were tested with a certain amount of palladium (II) hexafluoroacetylacetonate (Pd(hfa)<sub>2</sub>) at 150°C and 150 bar, with an impregnation time of 60 min. Electroless plating of the Kevlar fibres impregnated with Pd was performed in a conventional process with chemicals in an ultrasonic bath as described in paper [6]. It could be shown that after loading of 2wt% of the complex on the fibre about 10-12 g copper coating per m<sup>2</sup> could be deposited on the surface. Of course this is a quite expensive way to produce polymer fibres with electrical conductivity but after further development cheaper solutions will become available.

### Surface modifications of PET fibres with natural polymers [7]

Another very interesting surface modification for coating of PET fibres with natural polymers was suggested by Satoko Okubayashi. First the PET fibres are impregnated with cross linking substances by means of supercritical CO<sub>2</sub> similar to the above mentioned process. The cross linked substances react in the following step with natural polymers in a conventional water process.

For example the following textiles were produced:

- PET cloths with 1,1 wt% sericin
- PET cloths with 0,7 wt% collagen
- PET cloths with 1,0 wt% chitosan

The goal to produce cloths which are very eudermic was reached in most of the cases. Of course further research is necessary.

#### [7] Increase in wet ability of PET fibres by impregnation with polyethylenglycole

For some applications it is desired to increase the wet ability of PET fabric. One of the suggestions made by Satoko Okubayashi was to impregnate PET fibres with PEG#1000.

#### [7] Preparation of conductive PET fabrics by impregnation with pyrroles

A further possibility to produce PET fabrics with a uniform conductive layer is to impregnate fibres, moulded paddings or foils with pyrroles. Pyrroles are substances with a high content of carbons. In order to reach a uniform conductivity layer after polymerisation of the pyrroles a high content of pyrroles must be loaded on the material (up to 15wt%). The polymerisation is performed in a  $\text{FeCl}_3$  solution as shown in Figure 4. After optimal polymerisation of the pyrroles an excellent adhesion between the layer and PET with a neglectable decrease in mechanical strength of the polymer can be reached. There is only a slight decrease in surface conductivity even after 20 or 30 times washing. The most interesting application is the preparation of antistatic polymer materials.

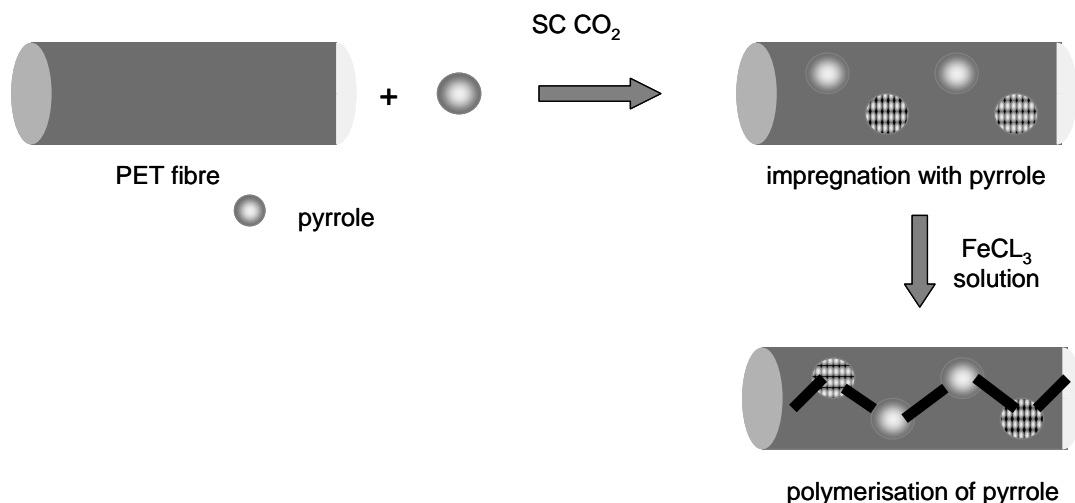


Figure 4. Preparation of conductive PET fabric with polymerised pyrroles

#### Surface modification of nylon fibres with a metal organic complex (mainly Titanium) to improve the UV-protection of technical textiles

Finally it should be mentioned that the resistance of the surface of fibres and foils against ultra violet light can be improved by impregnation with a titanium complex.

The main applications are the improvement of technical textiles, like window blinds or sail cloth for boats.

## IMPREGNATION OF CELLULOSE FIBRES AND AEROGELS [8]

In the 5 litres laboratory plant shown in Figure 5 various cellulose products were impregnated with active ingredients like vitamins and especially D-panthenol. Lyocell fibres were chosen to be impregnated with D-pantheol with the goal to produce seudermic textiles. After the impregnation the efficiency of the incorporation of D-pantheol in the cellulosic fibres and the resistance against multiple washing procedures were tested. Successful impregnation was confirmed with Raman spectroscopy. These investigations showed that the incorporation of D-pantheol into the fibres was successful. Nevertheless the amount of the active substance was lower on the surface of the fibre cross section compared to the concentration in the centre of the fibre. It can be assumed that the substance is washed off at the end of the treatment, when the autoclave is depressurized.

The incorporation of the substance in such a way that it resists common laundry procedures, which is important for the use of clothes, was less successful.

The test in a commercial washing machine showed that at 40°C most of the D-pantheol was removed during the washing process.

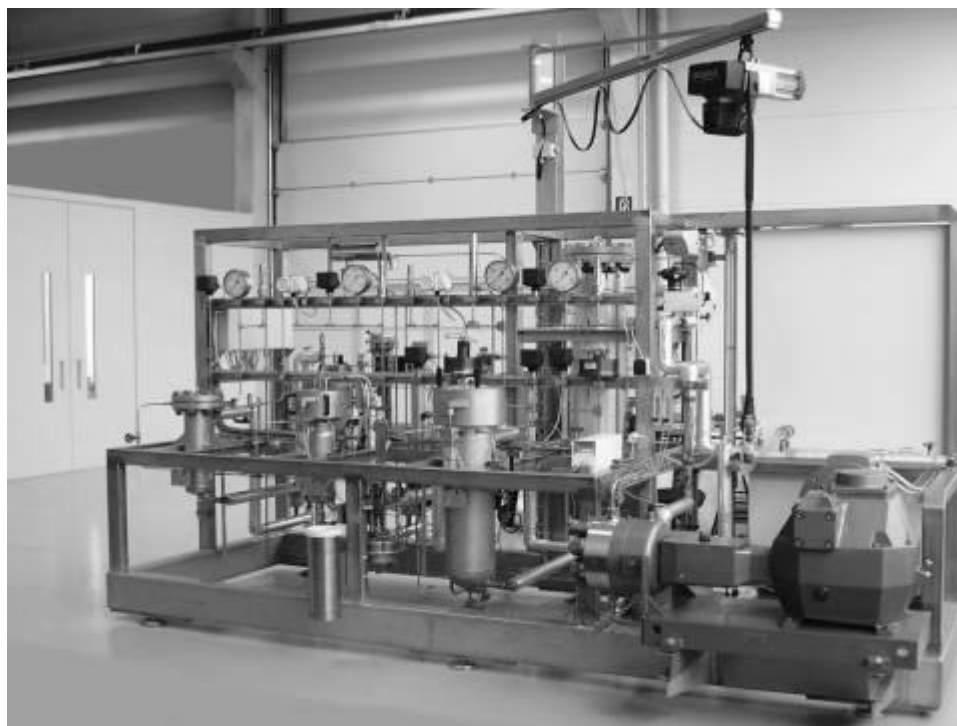


Figure 5. 5l/1000bar laboratory plant

In summary the impregnation of Lyocell fibres using the supercritical carbon dioxide process yields much better results compared to the steaming process, which is normally used to impregnate Lyocell fibres. The resistance against washing of in the laundry is not satisfactory. This means the product can only be used for single use applications. This one time usage could be interesting in the medical field for wound healing or for slow release of active substances to the skin and wounds.



## **IMPREGNATION OF POLYETHYLENE COMPONENTS USED FOR MEDICAL PURPOSES [9, 10, 11, 12]**

More than 2/3 of all hip- and knee endoprosthesis worldwide are equipped with articulated surfaces made of ultrahigh molecular weight polyethylene (UHMW-PE). This material has been successfully used for this application for 30 years. Lifetime is more or less limited to 10-15 years due to an oxidative degradation in vivo. By adding natural antioxidants like  $\alpha$ -tocopherol to the UHMW-PE this degradation can be slowed down. Cross-linked UHMW-PE has a much better stability, but  $\alpha$ -tocopherol cannot be mixed with the material before the cross-linking process. On the one hand  $\alpha$ -tocopherol acts as a radical scavenger hindering the cross linking process which leads to a material with lower network density and lower wear resistance. On the other hand a lot of the  $\alpha$ -tocopherol is degraded during the cross-linking process. UHMW-PE is cross-linked by electron beam irradiation followed by annealing. In the annealing process the UHMW-PE samples are stored for several hours at a temperature above the melting point in order to reduce the remaining free radicals.

Supercritical CO<sub>2</sub> is known for its high diffusion coefficient in polymers and offers one of the best solutions for impregnation of  $\alpha$ -tocopherol into UHMW-PE. The investigated impregnation conditions were 100 - 300 bar and temperatures of 140 - 170°C. According to the higher solubility of  $\alpha$ -tocopherol in high density CO<sub>2</sub> the optimal impregnation pressure was close to 300 bar. In some cases the samples were cooled down to 30 - 80°C after impregnation before depressurization started. After the treatment the polymer samples were cut into thin films (approx. 150  $\mu$ m), which were analysed by HPLC.

At lower temperatures the penetration depth was quite low, only 2-3 mm. By increasing the temperature close to the melting point of the polymer higher  $\alpha$ -tocopherol concentrations could be loaded into the polymer. But there were still big differences of concentrations between the surface and the centre of the polymer. In order to reach a more homogenous  $\alpha$ -tocopherol distribution the samples were annealed in nitrogen for several hours after impregnation. At temperatures of 160 - 200°C  $\alpha$ -tocopherol from the surface layer diffuses into the centre of the sample, resulting in a more homogenous distribution as shown in Figure 6.

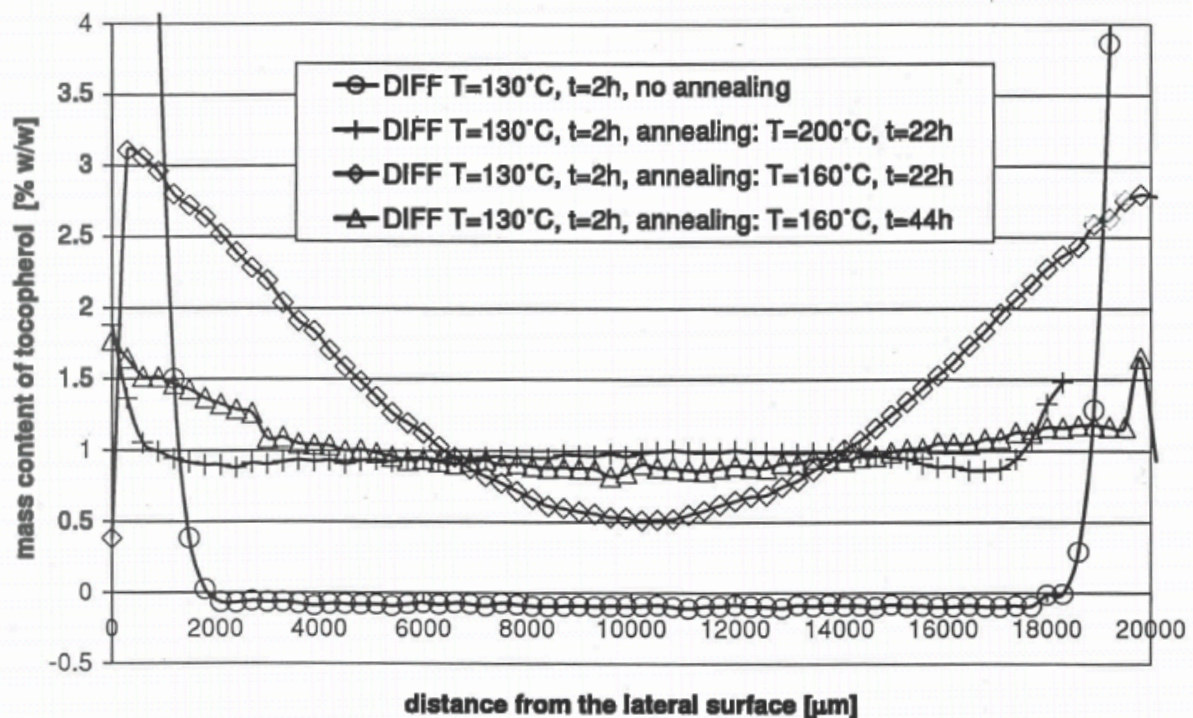


Figure 6. Homogenisation of the high edge concentration of  $\alpha$ -tocopherol after diffusion through annealing in inert atmosphere

In all process steps there must be a strict exclusion of oxygen in order to avoid any degradation of the UHMW-PE.

An experiment with original hip cups impregnated at 170°C and 300 bar for 12 hours resulted in a nearly homogenous distribution of approx. 1 wt%  $\alpha$ -tocopherol in the cup. These tests showed excellent results and were very satisfactory for the client.

## CONCLUSIONS

In the recent years many processes and applications using CO<sub>2</sub> impregnation have been developed. Unfortunately only wood impregnation has been realized on industrial scale so far, but also other processes are interesting for industry. NATEX can contribute to the commercial realization of additional applications by using its own R&D units and pilot plants for scale up tests and its accumulated know-how for equipment design. In the beginning primarily the reduction of solvents and waste water were the driving force for the development for new processes. Recently complete impregnation (surface and core of the material) plays a decisive role, which is possible based on the high diffusion velocity of supercritical CO<sub>2</sub>. This complete impregnation allows the creation of new material properties, which was not possible so far.

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