STERILISE IMPLANTABLE HIGH-TECH (BIO-) MATERIALS THE ECO-FRIENDLY WAY

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Introduction

As biomaterials become increasingly abundant in implant surgery the need for a low-temperature method has to be met. There are technologies based either on gamma irradiation [1] or toxic gases [2] that work efficiently below temperatures of 60 °C. The use of ETO (ethylene oxide) and formaldehyde is more than questionable from a safety and environmental point of view. Therefore it has been banned from use in hospitals in numerous countries [3]. The application of radioactive material naturally leads to radioactive waste resulting in economical and environmental issues.

Disinfecting textiles is important for a variety of industries. Implantable fabrics, however, inherently have to be sterile. High-pressure (HP) CO_2 treatment is a low-temperature technique for disinfection that is already in use for various liquid food products. Also for medical textiles it allows the combination of mild treatment parameters, thus protecting sensitive textures. Additionally, it is environmentally benign opposed to conventional processes.

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The first challenging task of this project was to verify the efficacy of the innovative process for inactivating vegetative pathogenic germs on textile products by applying (HP) CO_2. Secondly, complete sterilisation (including inactivation of persistent spores) for implantable fabrics had to be achieved by dissolving low concentrations of ozone (<< 1 % w/w) into CO_2. Short treatment times are realised due to good transport of O_3 by the dense medium CO_2 and significantly reduced surface tension in the supercritical state. Finally, it had to be shown, that the method is appropriate for delicate materials (especially biomaterials) as frequently used for implants.

Typical implantable fabrics comprise of e.g. meshes and yarns made of PVDF (polyvinylidenfluoride), PP (polypropylene) and PLA (polylactic acid). Until now, it has not been known how these materials can withstand the new process and whether surface or bulk is damaged during treatment, particularly, as the swelling capacity of CO_2 is well known. Sensitive measurement techniques like XPS (X-ray photoelectron spectroscopy), contact angle, ATR-IR and DSC provide insight into surface morphology, -topography and –properties down to atomic level as well as information about changes in the bulk material.

Materials and Methods

The innovative process has been described elsewhere [4]. The investigated CO_2 pressure ranged from 50 to 100 bar and temperature was set to 25, 38 and 65 °C. Production of ozone and elimination after the treatment takes place on-site; furthermore, carbon dioxide can be recycled. Therefore, the innovative sterilisation is virtually a zero-emission process unlike most conventional methods. It requires neither handling of hazardous chemicals nor long quarantine storage of the treated implants.

The implantable meshes and yarns investigated are provided by the industrial partner FEG Textile Technology, Germany. However, most surface analytics were carried out on polymer films based on PVDF (a relatively strong, inert polymer), PP (which is, like PVDF non-biodegradable) and PLA (a polymer that is decomposed when implanted in the human body). Until now, it has not been known if these materials can withstand the new process and whether surface or bulk is damaged during treatment.

The dynamic contact angle was measured with distilled water as wetting agent (72,8 mN/m) It was evaluated using the Tensiometer K14 (Krüss, Germany) applying Wilhelmy plate method. We also measured contact angle with ethylene glycol, p.a. (Fluka, Germany) which has as surface tension of 47,7 mN/m and diiodo-methane 99% (Sigma-Aldrich, Germany) with a surface tension of 50,8 mN/m in order to determine the surface energy of the polymer which was calculated by linear fit applying Owens-Wendt model.

XPS provided insight into chemical surface composition and state of chemical bonding down to a depth of 10 nm. In this work a XPS apparatus type Ultra Axis (Kratos Analytical, UK) was applied.

In order to investigate the film surfaces morphology an Atomic Force Microscope (AFM) type D3100 (Digital Instruments, USA) was used as imaging tool. The topography of samples were studied in tapping mode. The cantilever (ULTRASHARP NSC16/50, MikroMasch, Estonia) had a normal spring constant of 35 N/m, a tip cone angle of 20 degrees, radius of 5~10 nm and modulus of 160 GPa to assure good imaging resolution.

Using Attenuated total reflectance Fourier-Transform Infrared Spectroscopy (ATR-FT-IR) insights were gained into chemical changes that resulted from the treatment. An IR Prestige-21 (Shimadzu, Germany) scanned a range from 600 – 4000 cm^{-1}at a mirror speed 2.8 and a resolution of 2.0 averages of 40 scans were calculated. Method for apodisation was Happ-Genzel.

With a Differential Scanning Calorimeter (DSC) the glass-transition and melting temperatures were investigated to identify treatment effect. Using a DSC 204 Phoenix (Netzsch, Germany) two cycles were applied to the sample with linear heating and cooling at a rate of 10 K/min.

A Scanning electron microscope (SEM) type ABT-55 (Topcon, Germany was used to investigate detail images of the film surface and edges.

Results and discussion

Recent research at our institute has clearly shown that also pathogenic vegetative bacteria (*staphylococcus aureus, candida albicans*) can successfully be inactivated just by highly compressed carbon dioxide. The addition of small amounts (<< 1 % w/w) of ozone assured spore (*Bacillus stearothermophilus, Bacillus subtilis*) inactivation of up to 10^6 cfu/ml.

Thermo-mechanical fabric properties were not negatively influenced by CO_2 treatment but XPS measurements clearly show an oxidation of the PVDF surface by ozone. FTIR lead to the conclusion that carbonyl groups were formed on PP surface. Measurement of dynamic contact angle led to a slight hydrophilisation in the cases of PP and PLA. Conversely, it did not show any significant differences between untreated, CO_2 treated and ozone treated PVDF film,. Short treatment times can be realised due optimised diffusion and transport of O_3 by the dense CO_2 medium and significantly reduced surface tension in the supercritical state.

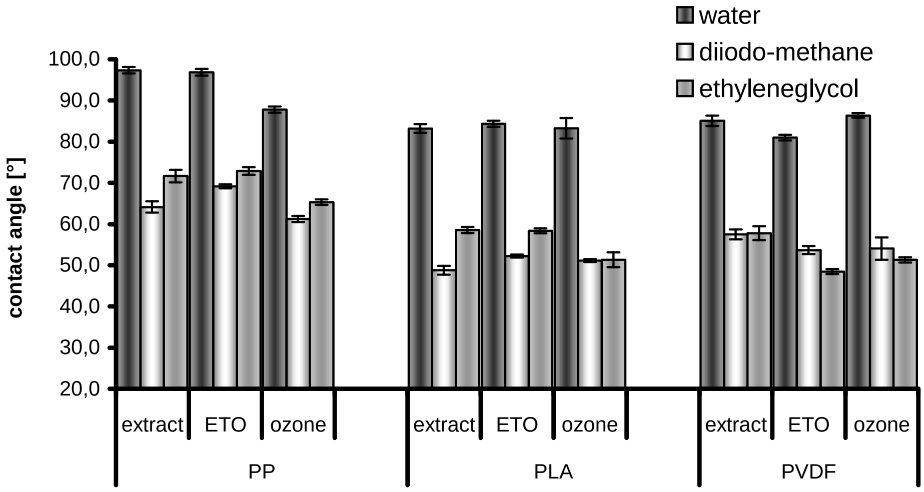

Fig. 1: Comparison of two sterilisation treatments on contact angle – ETO and HP-CO_2 – ozone technique.

Conclusions and outlook

The outcomes of this research show that HP-CO_2 in combination with O_3 can successfully be used to sterilise implantable textiles. It was shown that the inactivation of adherent biocontaminants is attainable in a low-temperature process and that even pressures as low as 50 bar can assure complete sterilisation of the textile material. Ongoing research is carried out on investigating fibroblast adhesion on the treated material. Further research also has to consider biocompatibility of the treated fabrics by applying cell-toxicity (LAL) test. Additional experiments focus on a better understanding of the underlying inactivation mechanisms.

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