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Cellulose Acetate / Hydroxyapatite Biocomposites: Synthesis and Characterization

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Abstract

This work presents a study on an alternative coating method based on biomimetic techniques which are designed to form a crystalline hydroxyapatite layer on porous cellulose acetate substrates. The porous scaffolds of the cellulose acetate were fabricated via solvent casting process. The Supersaturated Calcification Solution was used to investigate bone-like apatite formation on cellulose acetate matrix. The quality of the bioactive hydroxyapatite coatings was reproducible in terms of thickness and microstructure. The data suggest that the method utilized in this work can be effectively applied to obtain deposition of uniform coating of hydroxyapatite on porous cellulose acetate substrates.

Key words: *cellulose acetate, hydroxyapatite, biocomposites*

Introduction

Hydroxyapatite is the most important bioceramics materials for its unique bioactivity and stability. Naturally occurring and mostly available hydroxyapatite is hexagonal in structure with the chemical formula of one unit cell being $Ca_{10}(PO_4)_6(OH)_2$. Unlike the other calcium phosphates, hydroxyapatite does not break down under physiological conditions. It is thermodynamically stable at physiological pH and actively takes part in bone bonding, forming strong chemical bonds with surrounding bone. This property has been exploited for rapid bone repair after major trauma or surgery. While its mechanical properties have been found to be unsuitable for load-bearing applications such as orthopedics, it is used as a coating on load bearing implant materials such as titanium and titanium alloys or composites with polymeric materials [1-4].

Cellulose acetate is one of the most important synthetic organic esters because of its broad applications, such as in fibres, films, and membranes, and because it is made from cellulose, the most abundant biopolymer on earth. Cellulose acetate is inexpensive and most notably, it is biodegradable by certain microorganisms [5]. In recent years, natural cellulose materials have gained attention as phases for polymer composites [6-9].

This work presents a study on an alternative coating method based on biomimetic techniques which are designed to form a crystalline hydroxyapatite layer very similar to the process corresponding to the formation of natural bone. The hydroxyapatite formation on the surface of porous cellulose acetate support is investigated.

Experimental

Cellulose acetate (from Sigma Aldrich) with 39.8 % acetyl content was used as a membrane material. Acetone (from Merck) was used as solvent, formamide (from Merck) or water were used as non-solvents, whereas water was used as coagulation medium. Different solutions with various cellulose acetate polymer compositions were used for membrane preparation using phase - inversion method [10]. The morphology of samples was studied by Scanning Electron Microscopy (SEM) on Field Emission Scanning Electron Microscope (Fe-SEM) MIRA II LMU CS 01 TESCAN. The pore diameters have been determined by Bubble-point test (BPT) with a laboratory instrument. Further details on the materials processing and respective structural properties of membranes used in this study can be found elsewhere [10].

A simple supersaturated calcification solution (SCS) with high calcium and phosphate ion concentrations was used for biomimetic coating study. The SCS was prepared by dissolving the reagent grade chemicals, $CaCl_2 \cdot 2H_2O$, $NaH_2PO_4 \cdot H_2O$ and $NaHCO_3$ in deionised water successively. The ion concentrations of SCS solution are 4.0 mmol/L Na^+, 5.0 mmol/L Ca^{2+}, 10.0 mmol/L Cl^-, 2.5 mmol/L $H_2PO_4^-$, and 1.5 mmol/L HCO_3^-. In order to simulate the in vivo process, cellulose acetate membrane sample was immersed in SCS solution at 37 °C. The membrane samples were taken out of the solutions after 24 - 120 h immersion, rinsed with deionised water, followed by drying in air at 40 °C for 1 h. Hydroxyapatite formation on three dimensional scaffolds was investigated by X-ray diffraction (XRD, DRON 2.0 diffractometer, with a Cu Kα target) and by field emission scanning electron microscopy ((Fe-SEM) MIRA II LMU CS 01 TESCAN microscope).

Results and discussion

Cellulose acetate porous membranes prepared in our laboratory consist of three-dimensional polymeric structure, with pore sizes of molecular dimensions. The SEM images of the cellulose acetate membranes evidence the asymmetry/heterogeneity of these systems (Fig. 1a) [10].

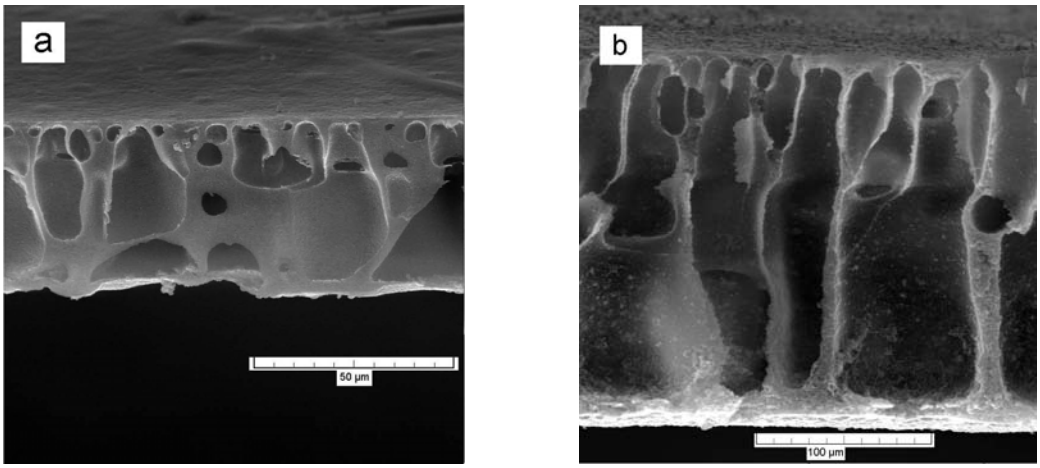

Fig. 1. SEM images of the cross-section of the cellulose acetate membranes: a) before [10] and b) after soaking in SCS for 120 h

Biomimetic treatment in SCS used in this study consisted in formation and deposition of hydroxyapatite layer on the active surface of cellulose acetate membranes. The hydroxyapatite formed on cellulose acetate membranes soaked in SCS was examined by field emission scanning electron microscopy and X-ray diffraction. In SEM picture of the cross-section of cellulose acetate membrane immersed in SCS, the hydroxyapatite deposits were observed (Fig.

1b). The hydroxyapatite crystals can be seen spread over the internal surface of the membrane. The structural characteristics of the coatings followed by XRD (Fig. 2) indicate the presence of hydroxyapatite on cellulose acetate surface. The XRD pattern for hydroxyapatite has many peaks in the range from about 7° to about 60° 2θ Cu Kα. The most intense peaks are in the range 30 to 45°, and the peaks are well defined, indicating the samples were well crystallized.

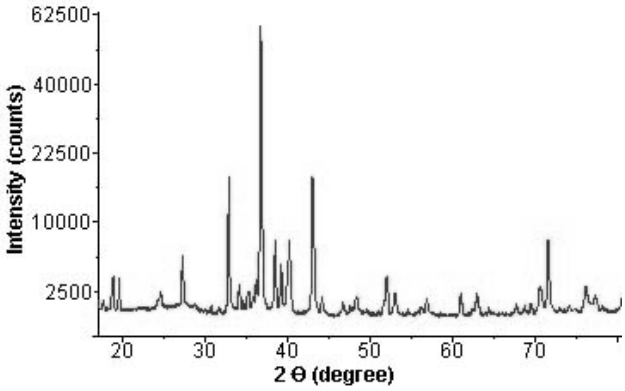

Fig. 2. XRD pattern of hydroxyapatite obtained on the membrane surface after soaking in SCS for 120 h

Sample immersed in SCS for 24 h have exhibited agglomerations of lamellar shaped hydroxyapatite crystals with a diameter of approximately 10 – 20 μm and many areas of noncoverage (Figure 3a). After 120 h soaking membrane in SCS, the surface of the sample is covered with a smooth, nano-textured hydroxyapatite layer about 10 μm thick (Figure 3b). This apatite layer exhibit the petal rose-like morphology observed in other studies [11].

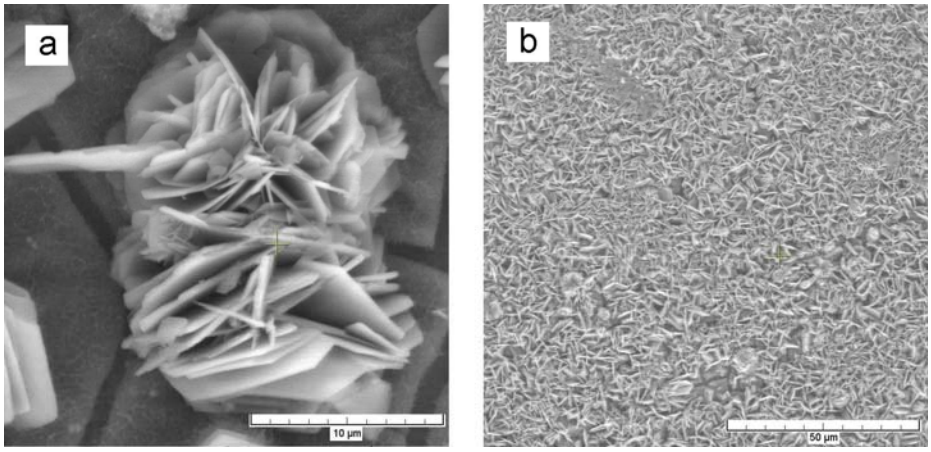

Fig. 3. SEM images of the membrane sample after soaking in SCS for 24 h (a) and for 120 h (b)

The formation of hydroxyapatite in the cellulose acetate surface is an indicator of its bioactivity. The data suggest that the method utilized in this work can be successfully applied to obtain deposition of coating of hydroxyapatite on cellulose acetate membrane.

Conclusions

The asymmetric porous cellulose acetate membranes can be fabricated by wet phase inversion method from a polymer / solvent / non-solvent casting system quenched in water. The SEM images of the cellulose acetate membranes evidence the asymmetry / heterogeneity of these

systems. The Supersaturated Calcification Solution (SCS) was used to investigate bone-like apatite formation on cellulose acetate matrix. The quality of the bioactive hydroxyapatite coatings was reproducible in terms of thickness and microstructure. SEM analysis showed that the hydroxyapatite layer thickness rapidly increased with increasing time in SCS. The data suggest that the method utilized in this work can be applied to obtain deposition of uniform coatings of nanocrystalline hydroxyapatite on porous cellulose acetate substrates.

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Biocompozite pe bază de acetat de celuloză şi hidroxiapatită: sinteză şi caracterizare

Rezumat

În lucrarea de față se prezintă un studiu privind posibilitatea depunerii de straturi subțiri de hidroxiapatită pe suporturi poroase de acetat de celuloză, apelând la o metodă biomimetică. Prin procedeul turnării au fost fabricate matrici (scaffolds) poroase pe bază de acetat de celuloză. Depunerile de hidroxiapatită pe suportul polimeric s-au realizat prin utilizarea de soluții supersaturate calcice. Pe baza rezultatelor obținute se poate concluziona că metoda aplicată este favorabilă obținerii de straturi subțiri şi uniforme de hidroxiapatită pe suporturi poroase pe bază de acetat de celuloză.