

# Polyurethane – Hydroxyapatite Bionanocomposites: Development and Characterization

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**Abstract:** In bone tissue engineering, bioactive glasses and related bioactive composite materials represent promising scaffolding materials. This work presents a study on an alternative coating method based on biomimetic techniques which are designed to form a nanocrystalline hydroxyapatite layer very similar to the process corresponding to the formation of natural bone. The hydroxyapatite formation on the surface of porous polyurethane is investigated. Three dimensional, porous scaffolds of the polyurethane were fabricated via solvent casting process. Hydroxyapatite formation on three dimensional scaffolds was investigated by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The quality of the bioactive hydroxyapatite coatings was reproducible in terms of thickness and microstructure. SEM analysis showed that the HA layer thickness rapidly increased with increasing time in SCS. The data suggest that the method utilized in this work can be successfully applied to obtain deposition of uniform coatings of nanocrystalline hydroxyapatite on porous polyurethane substrates.

**Keywords:** polyurethane, hydroxyapatite, composite, biomaterials characterization

## 1. Introduction

In bone tissue engineering, bioactive glasses and related bioactive composite materials represent promising scaffolding materials. The progress of synthetic materials and their use in tissue engineering applications has paying attention much interest in recent years. Typically, biomaterials can be divided into: polymers, metals, ceramics and natural materials. Composite biomaterials are produced by combining two or more of these fields. The combination of polymeric and ceramic materials could improve the mechanical properties of the material and enhance its biological properties. Currently, there are a number of strategies for developing bone tissue engineering scaffolds. The composite strategy provides a means for achieving stronger and bioactive scaffolds as compared to conventional polymer scaffolds[1,2].

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  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . 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 other materials [3-6].

Hydroxyapatite layer has been characterized to be similar to the mineral phase in human bones.

The bone tissue has two distinct structural forms: dense cortical bone and cancellous bone. The material of cortical and cancellous bone consists of cells in a mineralized matrix. All skeletal cells are known to differentiate from the mesenchymal stem cells of the embryo. In addition to mesenchymal stem cells, three principal cell types are present in bone: osteoblasts, osteoclasts and osteocytes. Osteoblasts are active bone forming cells and are present at the bone surface [7-9]. The bonding process between implant hydroxyapatite layer and natural bone is similar to the bonding between natural bones [11-13].

In the last years, a broad variety of synthetic polymers like polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP) and siliconic polymers (PS) have been used in medicine. Also, because of their biocompatibility and degradability, the polyurethanes (PU) are recommended as adhesives, membranes for dialyse, in cardio-vascular surgery as vascular protheses, artificial heart components, orthopaedic protheses etc.

Apatite-polymer composites have attractive features as candidates for novel bone substitutes for the reason that they may show bone-bonding capacity and mechanical performances derived from the organic substrate. As a method for fabrication of such a hybrid, Kokubo et al. proposed a biomimetic process that induces apatite formation on the surfaces of organic substrates at ambient conditions in a simulated body fluid with ion concentrations similar to those of human extracellular fluid, or related solutions supersaturated with respect to the apatite [14, 15]. Release of calcium ions ( $\text{Ca}^{2+}$ ) from the materials enhances apatite nucleation due to an increase in the degree of supersaturation of the fluid with respect to apatite [16].

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

## 2. Experimental

The polyurethane membranes were prepared using polyurethane (PU) and cellulose acetate (CA) polymers and N,N-dimethylformamide (DMF) as solvent. The membranes were prepared by casting a solution containing calculated amounts of PU and CA polymers on a glass plate and allowing the solvent to evaporate under caloric radiation. Further details on the materials processing and respective structural properties of membranes used in this study can be found elsewhere [17].

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,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{NaHCO}_3$  in deionised water successively. The ion concentrations of SCS solution are 4.0 Mmol/l  $\text{Na}^+$ , 5.0 Mmol/l  $\text{Ca}^{2+}$ , 10.0 Mmol/l  $\text{Cl}^-$ , 2.5 Mmol/l  $\text{H}_2\text{PO}_4^-$ , and 1.5 Mmol/l  $\text{HCO}_3^-$ . In order to simulate the in vivo process, polyurethane membrane samples were directly immersed in SCS solution at 37 °C. The membrane samples were taken out of the solutions after 24 - 72 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  $\text{Cu K}\alpha$  target) and by field emission scanning electron microscopy (FE-SEM, MIRA II LMU CS 01 TESCAN microscope). Also, all samples were characterized in transmission by Fourier transform infrared spectrometry (FTIR) using Perkin Elmer Spectrum 100 FTIR spectrometer.

## 3. Results and discussion

Much research has been dedicated to the coating of orthopedic and dental implants with porous ceramics, such as hydroxyapatite to increase hard tissue integration in vivo. Chemical immersion in SCS solutions have been shown to obtain apatite coatings on the order of 10 - 50  $\mu\text{m}$  of thickness, which are very homogenous and would be more favourable to biological interaction [18].

Biomimetic treatment in SCS used in this study consisted in formation and deposition of hydroxyapatite layer on the active surface of polyurethane membrane.

The polyurethane membranes used in this study have on asymmetric structure consisting of the dense top layer (active layer) supported by the porous sub-layer (sub-structure). The top layer is a thin and dense permselective skin. The thick sub-structure of the membrane consists of a band of intermediate density (the transition layer) consisting of widely open pores and a band of open-macro-

voids (Fig. 1a). The hydroxyapatite formed on polyurethane membranes soaked in SCS was examined by field emission scanning electron microscopy and X-ray diffraction. In SEM picture of the cross-section of PU membrane immersed in SCS, the hydroxyapatite deposits were observed (Fig. 1b). Hydroxyapatite crystals can be seen spread over the internal surface of the membrane. The structural characteristics of the coatings followed by XRD (figure not shown) indicate the presence of hydroxyapatite on polyurethane surface.

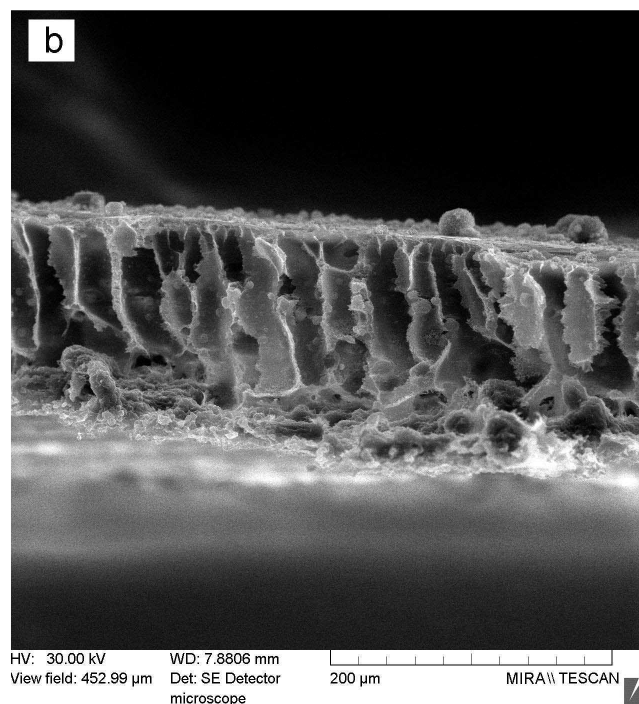
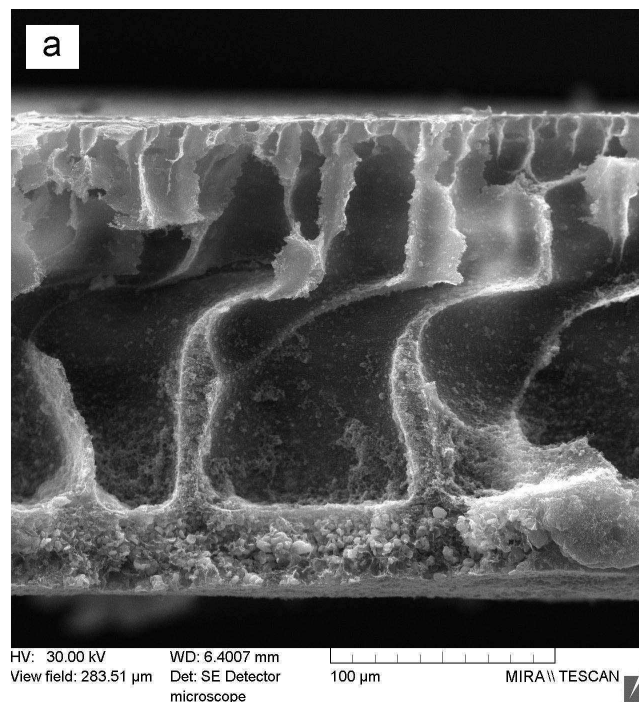


Figure 1. SEM images of the cross-section of the membrane sample before (a) and after soaking in SCS for 72 h (b).

Figure 2 depicts the SEM photomicrographs of the coated surfaces polyurethane membrane samples as a function of coating time.

Sample immersed in SCS for 24 h have exhibited agglomerations of lamellar shaped hydroxyapatite crystals with a diameter of approximately 1 - 2  $\mu\text{m}$  and many areas of noncoverage (Figure 2a). After 72 h soaking membrane in SCS, the surface of the sample is covered with a smooth, nano-textured hydroxyapatite layer about 10  $\mu\text{m}$  thick (Figure 2b). This apatite layer exhibit the petal rose-like morphology observed in other studies [19].

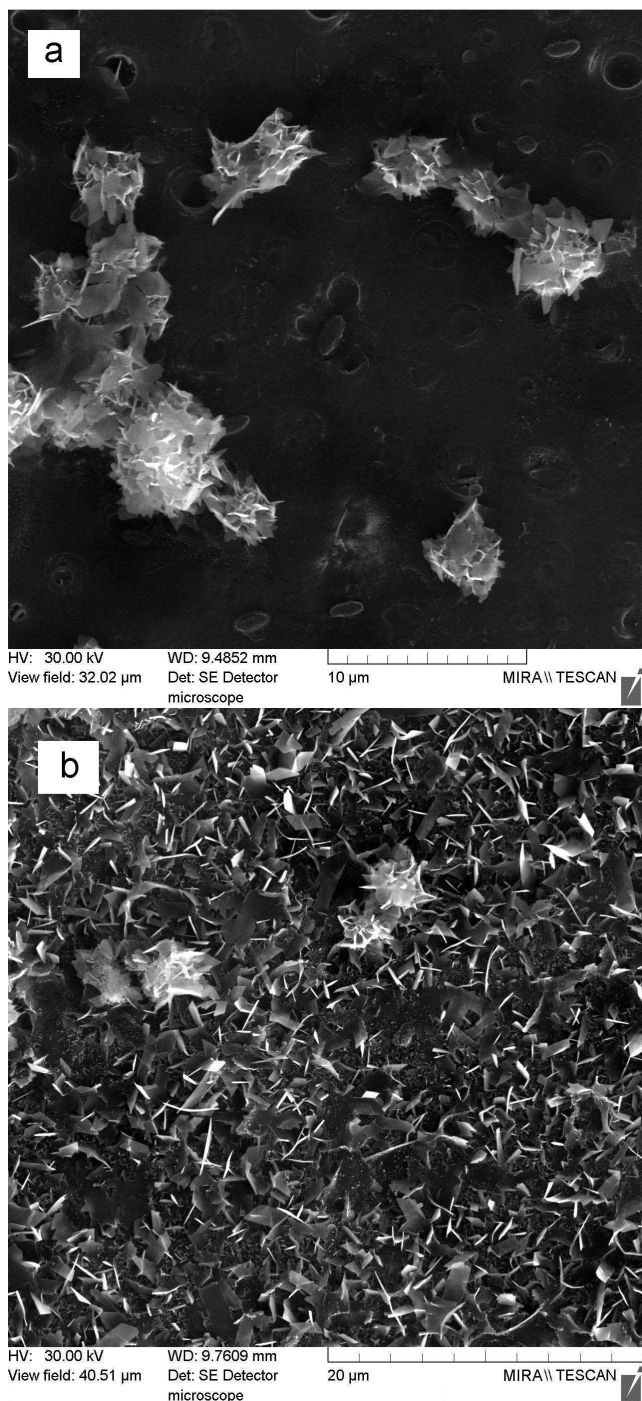


Figure 2. SEM images of the upper side of the membrane sample after soaking in SCS for 24 h (a) and for 72 h (b).

FTIR spectra of samples prepared after incubation in SCS show the existence of hydroxyapatite layer (Fig. 3).

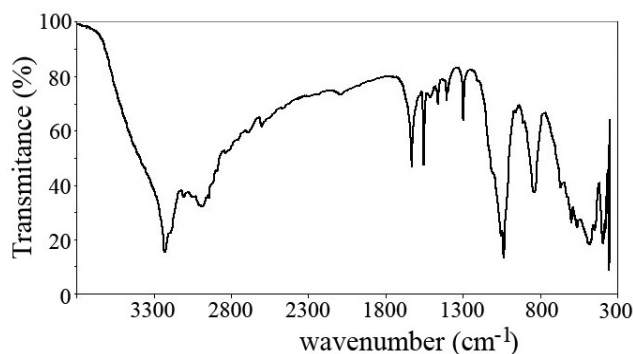


Figure 3. FTIR spectrum of hydroxyapatite formed on membrane sample after incubation in SCS for 24 h.

The bands at  $603\text{ cm}^{-1}$  and  $569\text{ cm}^{-1}$  were assigned to the O-P-O bending mode. The bands in the  $1000 - 1200\text{ cm}^{-1}$  region, due to  $\text{PO}_4^{3-}$  groups, are characteristic to hydroxyapatite, while the band at  $1600\text{ cm}^{-1}$  is due to the absorbed water.

The formation of hydroxyapatite in the polyurethane 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 polyurethane membrane. Future work will focus on the optimization of the composite scaffold for bone tissue-engineering applications and the evaluation of the 3-D composite in an in vivo model.

## 4. Conclusions

Three dimensional, porous scaffolds of the polyurethane were fabricated via solvent casting process. The Supersaturated Calcification Solution (SCS) was used to investigate bone-like apatite formation on polyurethane 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 successfully applied to obtain deposition of uniform coatings of nanocrystalline hydroxyapatite on porous polyurethane substrates.

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