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Bioactive coatings by vaterite deposition on polymer substrates of different composition and morphology

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Abstract

Calcium carbonate particles of vaterite crystalline structure were deposited on the surface of polymer substrates of different chemistry and morphology by a slurry dipping technique using ethanol as a solvent. Artificial prosthetic fibrous ligaments (polyester-based) and poly(ε-caprolactone) (PCL) 3-dimensional foams of high porosity were selected as model polymer substrates. The vaterite coated polymers were immersed in simulated body fluid to induce the formation of homogeneous hydroxycarbonate apatite (HCA) layers on the polymer surfaces, which were detected by SEM and XRD. The method offers great potential for inducing bioactive behaviour to normally bioinert polymers. In this investigation, fibrous structures for orthopaedic ligaments and 3-D porous tissue engineering scaffolds were considered and the application of the vaterite coating technique demonstrated.

Keywords: Bone tissue engineering; Biodegradable polymers; Artificial ligaments; Bioactivity; Calcium carbonate; Hydroxyapatite

1. Introduction

Synthetic polymers such as poly(α-hydroxyesters) have found applications in orthopedic devices, as implantable drug delivery systems and in tissue engineering scaffolds [1,2]. However these polymers may elicit an inflammatory response in the host tissue because of the release of acidic degradation products [3]. To overcome this problem, diverse approaches to the development of bioresorbable and bioactive composites for biomedical applications, including tissue engineering scaffolds, are being investigated, based on combinations of biodegradable polymers with hydroxyapatite or bioactive glasses in various scaffold architectures [4,5].

Much attention has been paid also to hydroxycarbonate apatite (HCA) as an interesting biomaterial. HCA is very similar to the apatite phase in living bone in its chemical composition and crystalline structure and has the ability to form a chemical bond directly with natural bone. Therefore, in addition to exhibiting good bioresorbability, HCA is a bioactive material [6,7]. HCA coatings on the surface of synthetic biodegradable polymers are likely to be a very convenient alternative for formation of scaffolds for bone tissue engineering, as well as for bone substitute materials and other orthopaedic devices.

A preparation method for HCA coatings based on immersion in SBF, which is a tris-buffer solution with inorganic ion concentrations almost equal to those of human plasma, has been introduced and termed a biomimetic coating method [8]. The incorporation of calcium carbonate ($CaCO_3$) particles, in vaterite crystalline form, as filler or coating onto polymer matrices has been shown to be highly effective in promoting the biomimetic formation of HCA coatings upon immersion of the materials in SBF [9–11]. In our previous work, HCA coatings on the surface of bioresorbable scaffolds for bone tissue engineering were produced using 3-D macroporous poly(DL-lactide) (PDLLA) foams impregnated by vaterite combined with simply immersion in SBF [11]. In the present investigation the possibility of producing HCA coatings on polymer

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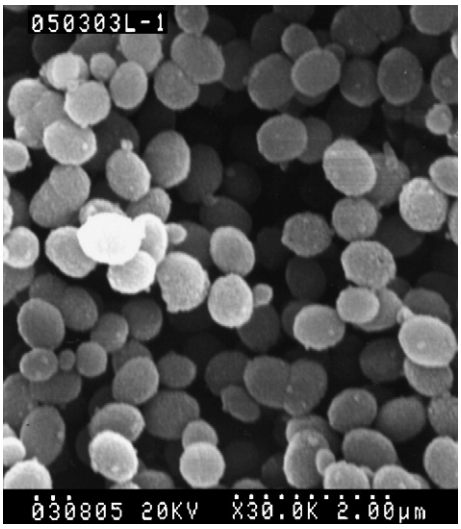

Fig. 1. SEM image of vaterite particles used in this investigation.

substrates of different morphology and composition has been explored by using selected polymer substrates impregnated by vaterite.

Artificial prosthetic fibrous ligaments (polyester-based) and poly(ε-caprolactone) (PCL) foams of high porosity were selected as model polymer substrates of different composition and two different morphologies, e.g. textile and foam-like structures, respectively. In case of prosthetic ligaments, an initial attachment between bone and ligaments plays an important role after anterior cruciate ligament reconstruction [12]. Thus, bioactivity of ligaments, e.g. the achievement of a surface able to bond to bone needs to be improved, which can be achieved by a tailored surface modification such as a HCA coating. PCL is a biocompatible polymer with suitable mechanical properties which is being considered for a variety of biomedical applications, including 3-D scaffolds for tissue engineering [13,14]. Composites made of PCL structures with HCA layers formed on their surfaces are useful as scaffolds for bone regeneration, due to the bioactivity function imparted by the HCA layers leading to intimate bonding with new bone tissue.

2. Experimental procedures

Vaterite was prepared using a carbonation process [15]. Briefly, the suspension was prepared by adding 200 g of Ca $(OH)_2$ and 100 g of distilled water into 2 L of methanol. CO_2 gas was blown for ~2 h at a flow rate of 2 L/min into the suspension at 20 °C. Gelation occurred by introducing CO_2 gas into the suspension. After gelation, the obtained particles were gathered by filtration and dried at 110 °C to prepare fine-sized powders. The BET surface area was measured to be ~70 m^2/g. Fig. 1 shows a scanning electron microscopy (SEM) image of the powders. The SEM image shows that the vaterite particles are in average <~0.5 μm.

Keio-Leeds® ligaments made from ICI Terylene 113 high tenacity polyester (polyrthlene terephthalate) were used (Xiros 28-30 Blenheim Terrace, Leeds, UK). Fig. 2(a) shows a SEM image of the ligaments used. PCL foams for bone tissue engineering scaffolds were fabricated by a thermally induced phase separation (TIPS) process, also termed freeze-drying. Fig. 2(b) shows the typical microstructure of the foams used. The TIPS process has been described in detail [16]. Pre-treatment of these polymers with ethanol was carried out at room temperature for 1 h, following a procedure originally described by Mikos et al. [17].

Vaterite deposition on polyester ligaments and PCL foam samples was carried out by a slurry-dipping process. For preparation of the dipping suspensions 1 wt.% of vaterite powder was added to ethanol. An alcohol was used as a solvent for preventing the fast dissolution of vaterite in water. The concentration of the slurry was determined by an optimization process based on a trial-and-error approach to achieve satisfactory results in terms of structural stability of the coating and adequate infiltration of the vaterite particles into the ligaments textile structure and the pores of the foams. The suspensions were stirred for 10 min before immersion of the polymer substrates. The pre-treated polymer samples were dipped into the prepared slurry for 3 min. The samples were then withdrawn at a velocity of 5 cm/s, and subsequently dried at room temperature in air atmosphere for 24 h and stored in desiccators for further studies. The prepared and dried vaterite/Keio-Leeds® ligament composites and vaterite/PCL composite foams were soaked at 37 °C in SBF consisting of 2.5 mM of Ca^{2+}, 142.0 mM of Na^+, 1.5 mM of Mg^{2+}, 5.0 mM of K^+, 148.8 mM of Cl^-, 4.2 mM of HCO_3^-, 1.0 mM of HPO_4^{2-}, and 0.5 mM of SO_4^{2-} [8]. The SBF solution also included 50 mM of

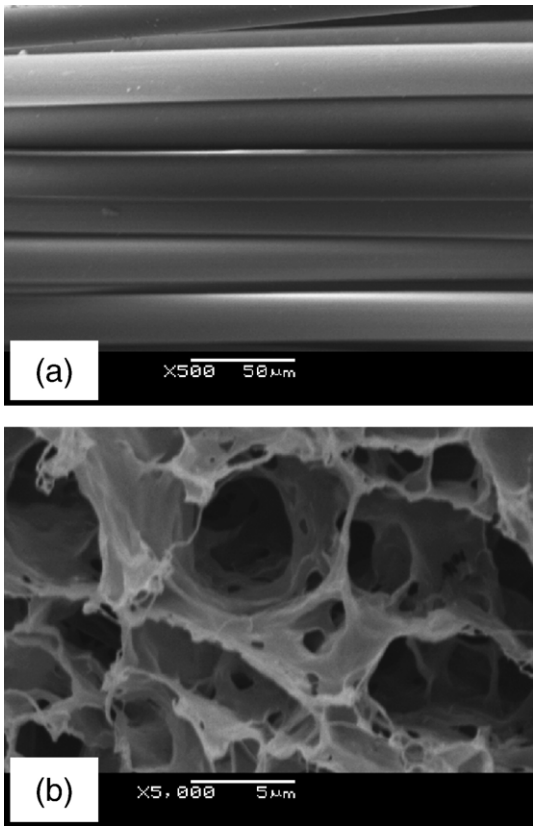

Fig. 2. As-received (a) Keio-Leeds® ligaments and (b) PCL foams obtained by TIPS, used in this investigation.