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Simple surface modification of poly(ε-caprolactone) for apatite deposition from simulated body fluid

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Abstract

Poly(ε-caprolactone) (PCL) with a bone-like apatite layer bound to its surface could be useful as a scaffold for tissue engineering applications. In the present study, the surface of PCL was treated with aqueous NaOH to introduce carboxylate groups onto the surface. The NaOH-treated material was subsequently dipped in aqueous $CaCl_2$ and $K_2HPO_4 \cdot 3H_2O$ alternately three times to deposit apatite nuclei on the surface. The surface-modified material successfully formed a dense and uniform bone-like surface apatite layer after incubation for 24 h in simulated body fluid with ion concentrations approximately equal to those of human blood plasma.
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1. Introduction

The development of biomaterials applicable to tissue engineering technology has recently focused on the surface design of biodegradable scaffolds that can promote tissue regeneration. A biodegradable synthetic polymer coated with bone-like apatite on its surface is likely to be useful as a scaffold for bone regeneration, since apatite is a major inorganic component of natural bone, and exhibits good biocompatibility and osteoconductivity [1,2]. Various coating techniques for deposition of apatite on the surfaces of polymeric materials have been developed over the past two decades [3–9]. For example, Taguchi et al. proposed an alternate soaking process [4,5], in which a polymer substrate is alternately and repeatedly soaked in calcium ion and phosphate ion solutions. The apatite formed by this process is, however, rather different from bone apatite in its composition and structure [10]. Apatite that is similar to bone apatite can be obtained if it is deposited from a simulated body fluid (SBF) [11] with ion concentrations approximately equal to those of human blood plasma [12].

On the basis of this background, attempts to prepare a bone-like apatite–polymer composite have been made using a biomimetic process [7–9] in which the polymer surface is modified with functional groups effective in inducing apatite nucleation, and then immersed in SBF. Si–OH [7], Ti–OH [8], and carboxyl or carboxylate [9] groups have been used as the functional group. The mechanism of apatite formation on the surface-modified polymer is believed to involve functional groups on the polymer surface inducing apatite nucleation in SBF. The induction period required for the apatite nucleation is dependent on the kind [13], number [6] and arrangement [8] of the functional groups. Once the apatite nuclei are

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formed, they grow spontaneously into a dense and uniform layer of bone-like apatite by consuming calcium ions and phosphate ions from the SBF, since SBF is supersaturated with respect to apatite [12]. Therefore, the period required for inducing apatite nucleation is a crucial factor in the apatite-forming ability of the polymer in SBF. If apatite nuclei could be previously introduced onto a polymer surface, the resultant surface-modified polymer would form a bone-like apatite layer on its surface within a short period in SBF. In this case, functional groups on the polymer surface would act as anchors between the polymer surface and apatite nuclei.

In the present study, modification of the polymer surface with carboxylate groups was attempted by surface modification of a biodegradable polyester using aqueous NaOH. The carboxylate-modified specimen was subsequently dipped alternately in calcium ion and phosphate ion solutions to deposit apatite nuclei onto its surface. The apatite-forming ability of the surface-modified specimen was examined in SBF. Poly(ε-caprolactone) (PCL) was selected as the biodegradable polyester, because it is biocompatible, mechanically strong and easily moulded [14]. The degradation rate of PCL can be varied considerably by the formulation or conditions of synthesis [15]. PCL and its copolymers have excellent mechanical and chemical properties that are appropriate for a variety of biomedical applications [16,17]. In the present case, a composite made of PCL with apatite formed on its surface could be useful as a scaffold for bone regeneration.

2. Materials and methods

2.1. Preparation of specimens

Two types of PCL specimen were prepared in the form of plates or porous scaffolds. A PCL plate, 1 mm in thickness, was prepared by hot-pressing PCL pellets (Aldrich Chemical Co. Inc., Japan, Average Mn = 80 000 (GPC)) at 70 °C. A matrix-type PCL scaffold was produced using a rapid prototyping technology known as fused deposition modelling [18,19]. The scaffold used in this experiment was produced by Mr. Kim Cheng Tan of the Temasek Engineering School, Temasek Polytechnic, Singapore. The PCL scaffold with a porosity of $65 \pm 3\%$ was produced with regular triangular pores as a result of a 0/60/120° lay-down pattern. The pore sizes of the scaffold were within the range of $380 \times 430 \times 590\,\mu m^3$. The PCL plate and scaffold were cut into square pieces, $1 \times 10 \times 10\,mm^3$ and $5 \times 5 \times 3\,mm^3$ in size, respectively. The specimen was ultrasonically washed with ethanol for 30 min, and dried under vacuum at room temperature for 24 h.

2.2. NaOH treatment

The PCL specimen was immersed in 5 mL of aqueous NaOH (Nacalai Tesque Inc., Japan) with concentrations of 0.1, 1, 5 and 10 M at 50 °C for 48 h at a shaking speed of 20 rpm. The specimen, removed from the NaOH solution, was washed extensively with ultra-pure water, and dried at room temperature in air for a few minutes.

2.3. Alternate dipping in calcium ion and phosphate ion solutions (CaP treatment)

The NaOH-treated specimens were dipped alternately in calcium ion and phosphate ion solutions by the following process (abbreviated as CaP treatment) [4,5]. Prior to the CaP treatment, the NaOH-treated specimen was connected on one of its corners to a platinum wire with a diameter of 0.5 mm. Using the wire, the specimen was dipped in 20 mL of 200 mM $CaCl_2$ (Nacalai Tesque) aqueous solution for 10 s, dipped in 20 mL of ultra-pure water for 1 s and then dried in air for a few minutes. The specimen was subsequently dipped in 20 mL of 200 mM $K_2HPO_4 \cdot 3H_2O$ (Nacalai Tesque) aqueous solution for 10 s, dipped again in 20 mL of ultra-pure water for 1 s and then dried in air for a few minutes. The dipping and withdrawal rate was fixed at 50 cm/min using a linear head motor equipped with a speed controller (Oriental Motor Co. Ltd., Japan). The above alternate dipping in calcium ion and phosphate ion solutions was performed three times at room temperature. The same $CaCl_2$ and $K_2HPO_4 \cdot 3H_2O$ solutions, and ultra-pure water, were used for a given specimen throughout the three cycles of alternate dipping.

2.4. Immersion in SBF

The NaOH-treated specimens and those further subjected to the CaP treatment were immersed in 30 mL of SBF [11] of pH 7.40 and ion concentrations (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM), approximating those present in human blood plasma, at 36.5 °C for 24 h. The SBF was prepared by dissolving NaCl, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 (Nacalai Tesque) in ultra-pure water and buffering to pH 7.40 at 36.5 °C with Tris(hydroxymethyl)aminomethane (final concentration of 50 mM) and aqueous 1 M HCl solution (Nacalai Tesque). The specimen, after removal from the fluid, was gently washed with ultra-pure water and then dried in air at room temperature for 24 h.

2.5. Surface characterization

The surface structures of the specimens were examined using an X-ray photoelectron spectrometer (XPS;

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