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Fabrication of nanostructured composites based on hydroxyapatite and ϵ -polylysine



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ABSTRACT

An objective of this work was to develop novel inorganic–organic nanocomposites based on the hydroxyapatite (HAp) and natural biopolymer ϵ -polylysine (ϵ -PL) as bone tissue engineering matrices. For this investigation, the composites with HAp/ ϵ -PL ratios of 50/50 and 70/30 by wt% were prepared through *in situ* precipitation of HAp in ϵ -PL aqueous solutions followed by spray drying of obtained suspensions. The FT-IR spectra and FE-SEM micrographs demonstrated that the composites were obtained in a form of spherical microgranules which consist of nanosized apatite crystallites interacted with ϵ -PL organic phase. The XRD patterns indicated that crystallization behavior of the HAp was affected by addition of ϵ -PL.

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1. Introduction

The development of biomaterials for tissue engineering is to create surfaces which can provoke specific cellular responses and direct new tissue regeneration [1]. Thus, inorganic/organic systems such as calcium phosphate (CaP)/natural biopolymers, including hydroxyapatite (HAp)/natural biopolymers, have attracted a great deal of attention over the past few years as a carrier for the delivery of antibiotics in the treatment of bone tissues.

ϵ -Polylysine (ϵ -PL), a kind of natural biopolymer, is water soluble, biodegradable, edible and nontoxic toward humans and environment. ϵ -PL is homo-poly-amino acid characterized by peptide bond between carboxyl and ϵ -amino groups of L-lysine [2]. Hence, amino groups and carboxyl functional groups provide opportunities in the preparation of nano-biocomposite and bioactive molecular attachment [2,3]. Moreover, ϵ -PL is a well-established cell adhesion promoter with excellent chemical functionality [3].

HAp is a major inorganic component of bone with excellent biocompatibility and bioactivity and thereby considered to be promising bone replacement material [3,4–7]. In recent years many attempts have been done for the fabrication of inorganic–organic composites based on crystallization of inorganic phase by organic substances [8–13]. Polymers containing polar functional

groups such as [–COOH], [–CH–], [–CH₂–], [–OH] have been found as ionizable side groups providing greater affinity to positive (Ca²⁺) ions and the nucleation of HAp crystals in the solution. Attempts in the *in situ* mineralization technique have been done by poly(lactic acid) [8], poly(acrylic acid) [9], poly(vinyl alcohol) [10], collagen [11], starch [12], gelatine [13] etc. Although significant work has been done investigating the interactions of various macromolecules with HAp, there is limited number of researches dealing with preparation of HAp/ ϵ -PL composites. Stupp et al. have developed bioactive materials known as organoapatites (OA), which are composed of HAp and organic macromolecules, where poly(amino acids), such as PL were used as an electrostatic coating on the surface of titanium to nucleate the formation OA crystals [6,7]. Recently the preparation of Zn-containing OA by the chemical modification of OA to introduce Zn ions into these materials have been reported [14]. Ding et al. have reported the preparation of novel hybrid nanoparticle of PL/HAp/carbon nanotube through precipitation method, which could be utilized to act as an ‘affinity template’ for protein immobilization [3]. However, previous works mainly report the development of ϵ -PL enhanced HAp coatings on metallic implants. Thus, the objective of this work was to develop novel methodology for the preparation of HAp/ ϵ -PL composites are envisioned for biomedical applications such as bone fillers, local drug delivery systems, bone tissue engineering matrices etc. The new material would combine abovementioned chemical and biological functionality, including antibacterial properties [2,3], of ϵ -PL and bioactivity of HAp. For

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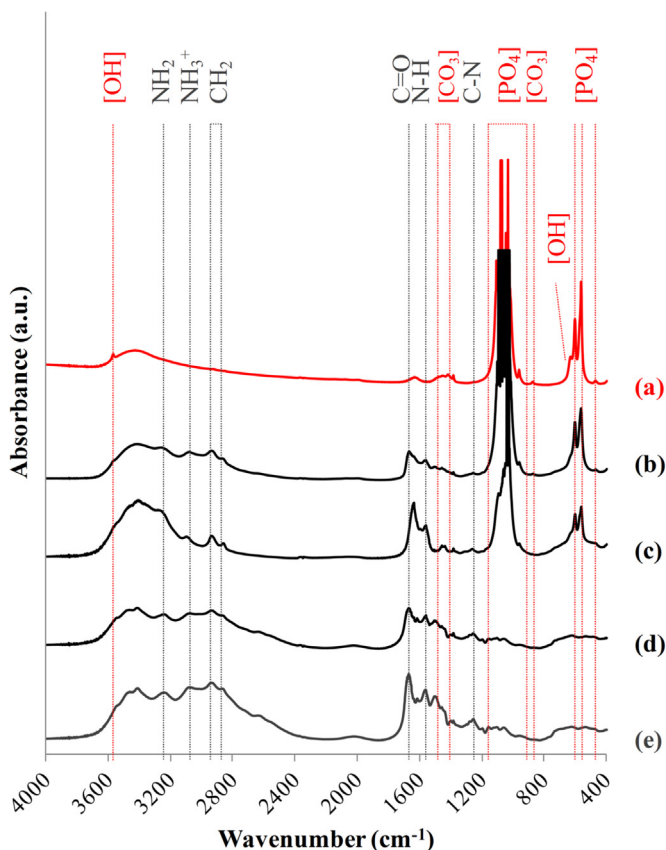


Fig. 1. FT-IR spectra of (a) HAp powder, (b) spray dried 70HAp/30ε-PL, (c) spray dried 50HAp/50ε-PL, (d) spray dried ε-PL, and (e) commercial ε-PL.

this investigation, composites with different HAp-to-ε-PL compositions were prepared. The effectiveness of the methodology was evaluated by Fourier transformation infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM).

2. Materials and methods

The ε-PL aqueous solution with concentration 5 wt% (ε-PL/water ratio) was prepared by fully dissolving ε-PL ($C_6H_{12}N_2O$, polymerization degree 25–35, Chengdu Jinkai Biology Engineering Co.) in deionised water at ambient temperature. HAp were synthesized with a stoichiometric Ca/P molar ratio of 1.67 in the presence of 5 wt% aqueous solution of ε-PL at concentration of 50 wt%, and 70 wt% (HAp/ε-PL ratio) by reacting 2 M H_3PO_4 (puriss., 75%, Sigma-Aldrich) with (Ca^{2+}) from CaO (puriss., Fluka) bound to the ε-PL matrix. The microgranules were obtained by spray drying method in Buchi Mini Spray Dryer B-290 at 200 °C.

The composites were examined using field emission scanning electron microscopy (FE-SEM, Mira/LMU/Inca Energy 350, Tescan) with incorporated energy dispersive X-ray spectroscopy (EDS) for morphology and chemical analysis, respectively. Specimens were coated with gold layer (thickness 15 nm) before FE-SEM analysis.

Functional groups of the composites were analyzed using FT-IR (Varian 800, Scimitar Series). FT-IR spectra were recorded in the range of 400–4000 cm^{-1} with spectral resolution 4 cm^{-1} and 30 times scanning.

Phase compositions of the composites were determined by XRD (Rigaku Ultima +) using $Cu K_{\alpha}$ ($\lambda = 1.5406 \text{ \AA}$) radiation produced at 40 kV and 30 mA with a step size of 0.06°, and a counting time of 200.025 s. For crystalline phase identification the

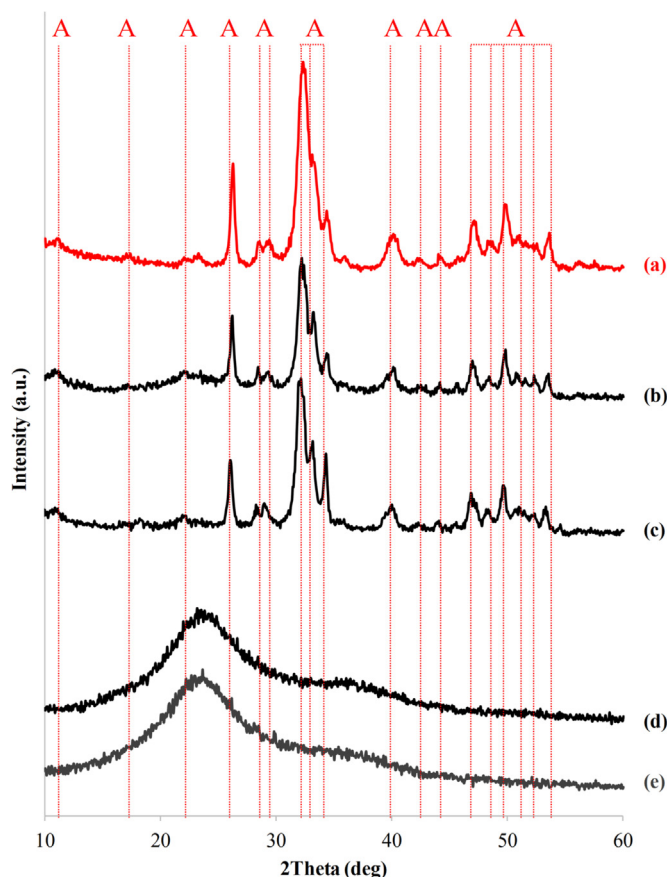


Fig. 2. XRD patterns of (a) HAp powder, (b) spray dried 70HAp/30ε-PL, (c) spray dried 50HAp/50ε-PL, (d) spray dried ε-PL, and (e) commercial ε-PL (A – apatite).

American Mineralogist Crystal Structure Database (AMCDS) was used (card #0001257 for apatite).

3. Results and discussion

FT-IR was employed to investigate the entrapment of apatite within ε-PL molecules. Fig. 1 shows overlaid FT-IR spectra from 4000 cm^{-1} to 400 cm^{-1} . The spectra (Fig. 1(d) and (e)) of raw ε-PL and the spray dried ε-PL showed similar FT-IR profile, indicating that the spray drying process did not degrade the chemical structure of commercial ε-PL. However, the intensity of the absorption bands of spray dried ε-PL has decreased. Therefore, indicating that drying-induced conformational alterations of the ε-PL may have occurred [15].

The predominant peak regions arising from the ε-PL were as follows: 3270 cm^{-1} , attributed to the unprotonated NH_2 and 3055 cm^{-1} , attributed to the (NH_3^+) ; 1672 cm^{-1} , attributed to the C=O stretching vibration from amide I bonds; 1565 cm^{-1} , attributed to the N–H bending vibration from amide II bonds, and 1257 cm^{-1} , attributed to the C–N stretching vibration from amide III bonds of the polypeptide [1]. The peak at 2924 cm^{-1} is assigned to CH_2 stretching vibration [1,3]. The acid [–COOH] and base [– NH_2] groups of amino acid can ionize in aqueous solution and become positively charged (cation) at low pH and negatively charged (anion) at high pH. Consequently, the carboxyl groups of ε-PL can provide nucleation sites for (Ca^{2+}) ions. Minor changes in the shape and the positions of C=O bands indicate structural and conformation changes occurring with addition of apatite phase related to building-in of (Ca^{2+}) ions in the polymer chain. Moreover, ε-PL has plentiful active amino groups, some of which could

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