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Fabrication of porous hydroxyapatite scaffold via polyethylene glycol-polyvinyl alcohol hydrogel state

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ABSTRACT

Hydroxyapatite (HAp) ceramic was prepared from $Ca(NO_3)_2\ 4H_2O$ and $(NH_4)_2HPO_4$ by co-precipitation method and HAp phase was stabilized up to 1250 °C. Porous HAp scaffold was fabricated by using polyethylene glycol (PEG) cross linked with polyvinyl alcohol (PVA). The fabricated scaffold has 70 vol.% porosity with strength 4.2 MPa and the major fraction of pores were found within the range ~70–100 μm diameter obtained by varying the amount and size of ceramic and PEG particles. XRD, FT-IR, SEM and mercury porosimeter techniques were used to study the phase purity, pore size and pore size distribution of scaffold. The molecular weight of PEG plays an important role in the morphology, microstructure, and pore size of scaffold. In-vitro bioactivity of the fabricated scaffold was studied in SBF (simulated body fluid) at pH ~7.4 and 37 °C.

1. Introduction

Hydroxyapatite ceramics were renowned as substitute materials for bone and teeth in orthopedic and dentistry field due to their chemical and biological similarity to human hard tissue [1]. A key component in tissue engineering for bone regeneration is the scaffold that serves as a template for cell interactions and the formation of bone-extracellular matrix to provide structural support to the newly formed tissue [2]. In scaffold, pores were necessary for bone tissue formation because they allow migration and proliferation of osteoblasts and mesenchymal cells, as well as vascularization [3]. In addition, a porous surface improves mechanical interlocking between the implant biomaterial and the surrounding natural bone, providing greater mechanical stability at this critical interface [4]. Since porous HAp is more resorbable and more osteoconductive than dense HAp, there is an increasing interest in the development of synthetic porous HAp, bones replacement materials for the filling of both load-bearing and non-load-bearing osseous defects [5]. Simulating the human bone structure, porous HAp scaffold has large surface area, which is beneficial for adhesion of biological tissue cells and growth of new bone phase [6]. The most common techniques used to create porosity in a biomaterial are salt leaching, polymeric sponge, gas foaming, gel casting and also incorporation of organic fugitives [7–11]. But in the above mentioned method the scaffold obtained does not have sufficient strength and pores are not well distributed. HAp scaffolds were fabricated through PEG–PVA particle hydrogel which results the interconnected porous structure through interpenetration between PEG and PVA particles. The hydrogel maintained interconnection of pores in the HAp matrix, which provides sufficient strength to the scaffold. The present research work aimed to develop macro porous HAp scaffold by the insertion of HAp powder into the PVA–PEG hydrogel and investigated the effect of concentration and molecular weight of the PEG particle on strength, porosity and pore size of synthesized scaffold.

2. Experimental

2.1. Synthesis of HAp powder

HAp powder was prepared by co-precipitation method using $Ca(NO_3)_2\ 4H_2O$ (Merck, India) and $(NH_4)_2HPO_4$ (Merck, India) as the starting materials and ammonia solution (Merck, India). A solution of 1 M $Ca(NO_3)_2 \cdot 4H_2O$ was prepared at 25 °C. Keeping Ca:P molar ratio for stoichiometric HAp = 1.67 constant, the amount of required $(NH_4)_2HPO_4$ was calculated and prepared by dissolving $(NH_4)_2HPO_4$ in deionized water. The prepared solution of $(NH_4)_2HPO_4$ was slowly added to the $Ca(NO_3)_2\ 4H_2O$ solution (in stirring condition). HAp particle was precipitated through NH_4OH at pH ~10. The HAp precipitate was continuously stirred for 2 h and aged for overnight for settling, followed by repeatedly washing

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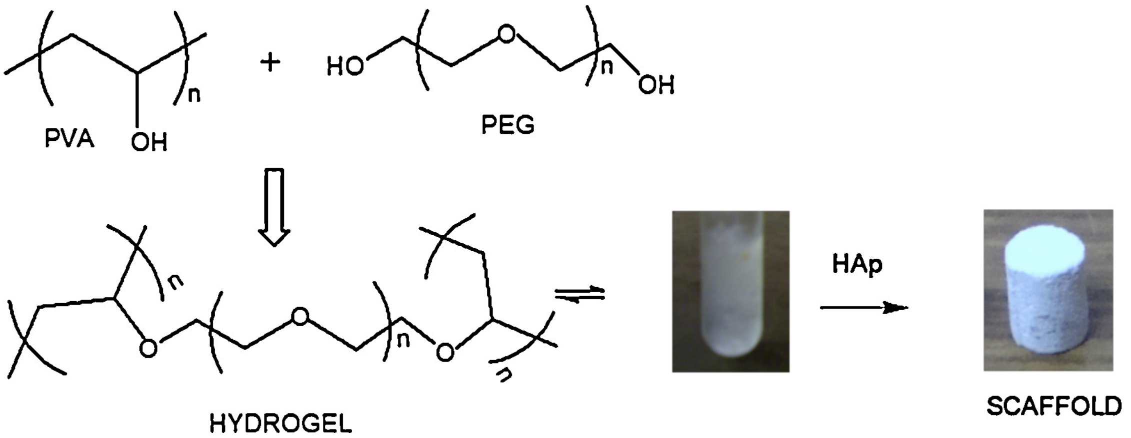

Fig. 1. Schematic representation of the formation of hydrogel between PEG and PVA.

with deionized water to remove ammonia and byproducts formed (NH_4NO_3). The chemical reaction leading to HAp formation is as follows:

$$10Ca(NO_3)_2 4H_2O + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 46H_2O$$

The centrifuge was carried out at a rotational speed of 8000 rpm. The resulting powder was dried at 80 °C and calcined at 850 °C for 2 h.

2.2. Characterization of HAp powder

Phase analysis of HAp powder was studied using the room temperature powder X-ray diffraction (Philips PAN analytical Netherland) with filtered 0.154 nm Cu K-α radiation. Samples were scanned in a continuous mode with a scanning rate of 0.02°/s. The HAp peaks were identified by referring JCPDS file (reference 74-0565). Moreover, the identification of functional groups in the HAp powder were also analyzed by standard FT-IR method (PerkinElmer RXI, Spectrum, USA) within the scanning range 4000–400 cm^{-1} applying KBr pellet technique. The surface area of powder were measure by BET surface area (Quanta chrome, Autosorb-I).

2.3. Preparation of porous HAp scaffold

The synthesized calcined HAp (40 wt.%) powder mixed with PEG (PEG 4000, PEG 6000, Merck India) in the weight % (20, 30 and 40) with respect to the ceramic to formed HAp-PEG slurry. The slurry was stirred for 2 h for well mixing. HAp-PEG slurry mixed with 10 wt.% PVA (Merck India) which formed hydrogel with PEG. PVA solution was prepared in deionized (DI) water (10 wt.% PVA) at 80 °C by constant stirring. After formation of a clear PVA solution, the solution was cooled down to 30 °C. The HAp slurry was cast into a glass mold. The demolded green HAp scaffold specimens were dried at 80 °C for 24 h and thermal annealing 1 h at 650 °C for the burn out of polymers and subsequently sintered at 1250 °C for 4 h at the rate of 3 °C per min.

2.4. Characterization of HAp scaffold

Surface morphology, microstructure, pore shape and pore size distribution of sintered HAp scaffolds were studied by SEM (JEOL JSM 6480LV). The SEM images of platinum coated sintered scaffolds were observed in secondary electron mode at 15 KV. The compressive strength of the synthesized scaffold samples was measured by universal testing machine (H10 KS TINIUS OLSEN) using the load cell of 10 KN with speed 2 mm/min. The cylindrical shaped HAp scaffold samples (14 mm diameter and 16 mm thickness) were broken in compression. Porosity of scaffold was

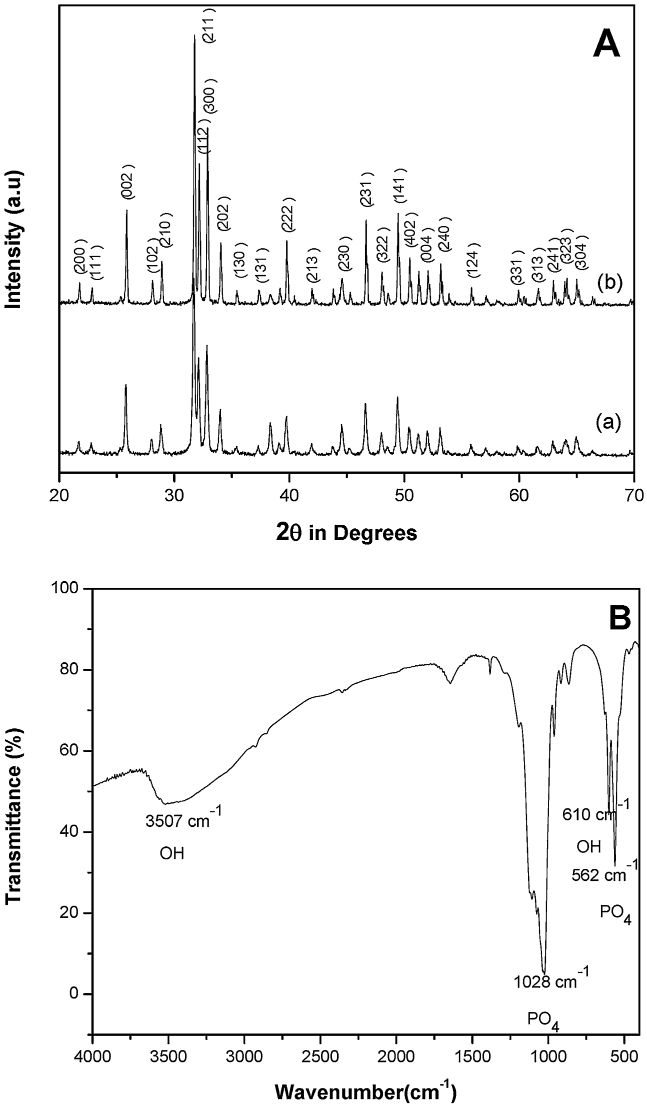

Fig. 2. X-ray diffraction pattern of calcined powder (850 °C for 2 h) (A(a)) and high temperature (1250 °C for 4 h) behavior (A(b)) and FT-IR spectrum of high crystalline HAp powder calcined at 850 °C for 2 h (B).