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Structure–property relationships of iron–hydroxyapatite ceramic matrix nanocomposite fabricated using mechanosynthesis method

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ABSTRACT

Hydroxyapatite (HAp) is an attractive bioceramics due to its similar composition to bone mineral and its ability to promote bone–implant interaction. However, its low strength has limited its application as load bearing implants. This paper presented a work focusing on the improvement of HAp mechanical property by synthesizing iron (Fe)-reinforced bovine HAp nanocomposite powders via mechanosynthesis method. The synthesis process was performed using high energy milling at varied milling time (3, 6, 9, and 12 h). The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and scanning electron microscopy (SEM). Its mechanical properties were investigated by micro-Vicker's hardness and compression tests. Results showed that milling time directly influenced the characteristics of the nanocomposite powders. Amorphous BHAp was formed after 9 and 12 h milling in the presence of HPO_4^{2-} ions. Continuous milling has improved the crystallinity of Fe without changing the HAp lattice structure. The nanocomposite powders were found in spherical shape, agglomerated and dense after longer milling time. The hardness and Young's modulus of the nanocomposites were also increased at 69% and 66%, respectively, as the milling time was prolonged from 3 to 12 h. Therefore, the improvement of the mechanical properties of nanocomposite was attributed to high Fe crystallinity and homogenous, dense structure produced by mechanosynthesis

1. Introduction

Over the past decades, hydroxyapatite (HAp) has been used in medical implant applications mainly as bone substitute and coating on metal or polymer implants [1,2]. Hydroxyapatite is mainly composed of calcium (Ca) and phosphorus (P) which can be found in human bone [3,4]. It is a bioactive material that promotes osseointegration, thus making it favourable for use on bone–implant interface [5,6]. Ions released during the dissolution of HAp stimulate the process of bone growth and remodelling [7]. This dissolution is more pronounced with amorphous HAp compared to crystalline HAp as reported by Xue et al. [7]. However, the brittle and low strength properties of HAp have been identified as the root cause for bone substitute and coating failures [8–10]. Attempts to overcome this limitation have been done recently, mostly by developing HAp composites. The HAp brittleness is ameliorated by incorporating titanium (Ti), mangan (Mn), and zirconium oxide (ZrO_2) into HAp, where this metallic reinforcement has improved HAp densification and crystallinity [9,11,12].

Iron (Fe) is another potential element to enhance the strength of HAp. It has been used as a framework structure for HAp bone filling device [13], and for improving HAp radiopacity in drug delivery applications [10,14]. Similar to Ti and Mn, Fe is added in HAp matrix as reinforcement for high compression resistance to inhibit failure over a range of deformation [13]. Previously, Fe–HAp composite was synthesized via wet-chemical method [11]. By wet-chemical method, Ajessh et al. [14] found that X-ray diffraction spectra of sintered iron oxide–HAp indicated the presence of intermediate phase which was responsible for the improvement of mechanical and biological properties of the HAp. However, the wet chemical method requires costly chemical reagents and involves long chemical routes [11]. Therefore, another feasible method to synthesis Fe–HAp composite by offers simpler and more direct process is required.

Mechanosynthesis is a direct mechanical route method [9], which is based on mechanical activation effect resulting from collided balls during milling step [15]. A work on CaP–Ti composite reported by Silva et al. [16] showed that increased in milling time has resulted in smaller grain size composite without reaching its melting point. This method also

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produced nano-size particles which is beneficial in providing large surface area for bone substitution and integration [17]. To this end, mechanosynthesis was chosen over wet-chemical method as a top-down synthesis from bulk material to smaller pieces using mechanical form of energy [17].

In this work, we aimed to synthesize 30 wt.% Fe–HAp ceramic nanocomposite using mechanosynthesis method at different milling times. Reinforcement of less than 15% Fe in hard matrix will not improve the mechanical property of HAp, while the reinforcement of more than 50% Fe will change the properties of HAp to metal behaviour [18]. Chang et al. [19] proved that 33 wt.% Fe was the optimum proportion for HAp reinforcement [19]. Therefore, 30 wt.% Fe was chosen and reinforced into HAp in order to improve its mechanical toughness while maintaining the HAp ceramic properties. The synthesized Fe–HAp nanocomposites were then subjected to several characterization analyses and mechanical tests to investigate the effects of milling time on the chemical functionality, crystallite size, lattice strain, morphology, and hardness.

2. Materials and methods

2.1. Sample preparation

Hydroxyapatite was prepared from bovine bone based on the work by Barakat et al. [6]. Firstly, portion of femur bones were taken from slaughtered cows, cut into 5 cm length, and cleaned with distilled water and acetone. The small bone pieces were boiled overnight and dried at 160 °C for 48 h to remove any fatty substances and impurities. Thermal decomposition was then performed on the dried bones through heating at 350 °C for 3 h to ensure that all fatty substances were removed. The bones were continuously heated at 750 °C for another 4 h to fully transform the bone into HAp. Finally, the chalky white HAp was crushed into powdered form by using mortar and pestle. By this stage, the powdered form of HAp is known as bovine hydroxyapatite (BHAp).

The 30 wt.% Fe–BHAp nanocomposite was prepared by adding 1.5 g Fe powders (particle size 450 μm, Goodfellow, UK) to 3.5 g BHAp. The powder mixtures were ball milled by using high energy milling (SPEX SamplePrep 8000M Mixer/Mill, USA) at 3, 6, 9, and 12 h (Fig. 1). The milling was operated with Teflon vial and zirconia balls. The ball ratio and rotational speed were set at 1:10 and 1200 rpm, respectively. The ball milled nanocomposite powders were then collected and stored in a desiccator for characterization and testing. The density of samples was measured by Archimedes method.

2.2. Characterization analyses

Chemical composition and crystalline phases of the nanocomposite powders were identified by an X-ray diffractometer (XRD, X'pert Diffractometer, Philips, USA) using CuKα radiation at λ of 0.15406 nm. Data were collected in 2θ range (20°–80°) at 0.05°/min. The diffraction peak analyses were conducted by using XPowder software (Ver. 2004.04.41 PRO, USA). Crystallite size and lattice strain were calculated based on Scherer's equations [15].

$$D = \frac{K\lambda}{(FWHM_{hkl}) \times \cos\theta} \quad (1)$$

$$E^2 = \frac{(FWHM)^2}{(4\tan\theta^2)} \quad (2)$$

where D is the crystallite size; K is the broadening constant (0.9); λ is the wavelength of X-ray beam; $FWHM$ is the full width at half maximum for the diffraction peak under consideration (rad); hkl is the Miller's plane family where (002) and (110) were applied for HAp and Fe, respectively; θ is the diffraction angle (°); and E is the lattice strain.

The presence of functional groups in the nanocomposite powders was investigated by Fourier transform infrared spectroscopy (FTIR, Prestige 21 Shimadzu, Japan). The FTIR spectra were obtained using KBr disks at 1:100 "sample-to-KBr" ratio. The transmittance spectroscopy range was set at 4000–400 cm^{-1} by 16 scans.

Morphology and particle size were then visualized by a field emission scanning electron microscope (FESEM, Zeiss Supra 35 VP,

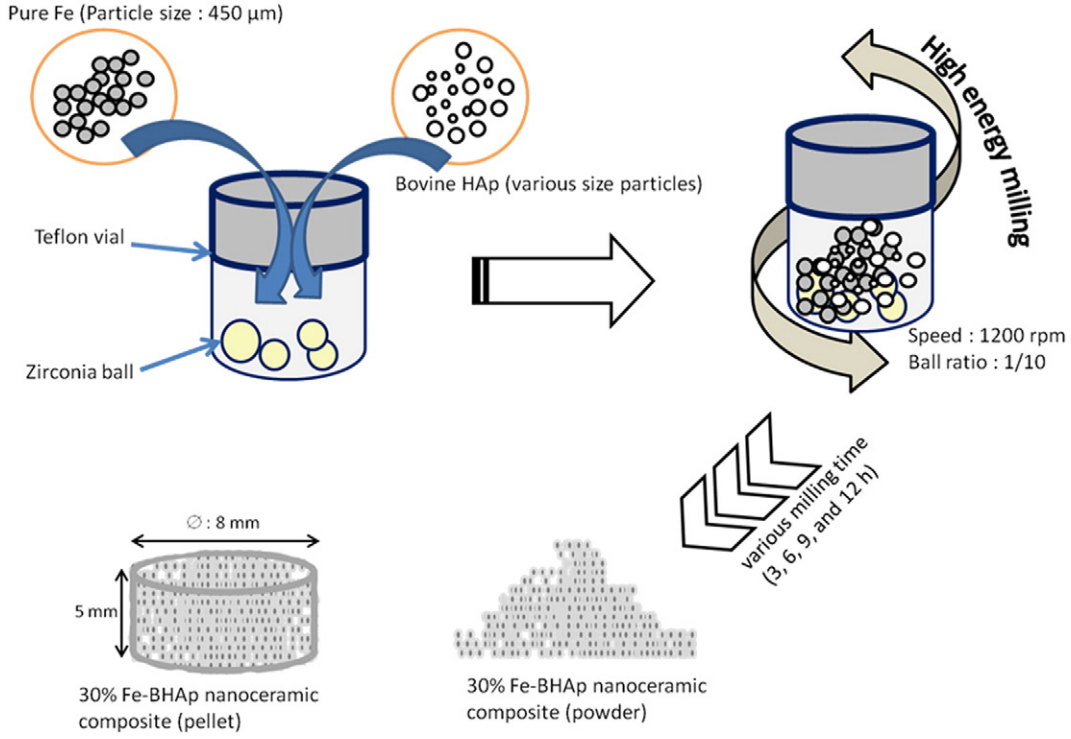

Fig. 1. Schematic view of mechanosynthesis method.