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Preparation of Zinc Doped-Biphasic Calcium Phosphate/Carbon Nanotube Composites

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ABSTRACT

Biphasic calcium phosphate (BCP) has been used in tissue engineering and orthopedicsdue to its good biocompatibility and osteoconductivity. However, its clinical applications are usually limited by the low strength and brittleness. The objective of this research was to develop Zn-doped BCP composites in which multi-wall carbon nanotubes (MWCNT) were introduced to the Zn-doped BCP ceramic matrix to improve the mechanical properties of the resulting composites. The starting powders have been synthesized via sol-gel method. Zinc concentration was varied in the range of 0, 1, 2, 4, 5, and 10mol%. After uniaxial pressing the compacted samples were sintered via conventional pressureless sintering. The samples were studied in terms of the phase stability, relative density, Vickers hardness, and fracture toughness as well as in vitro analysis in SBF solution. The results showed that hydroxyapatite as the main phase and β-tricalcium phosphate as the secondary phase of obtained powders. The morphology of the powders show the formation of nanocrystalline powder and individual particles are globular in shape.The maximum micro Vickers hardness and fracture toughness was achieved when fired at 1200oC, with 4.30 GPa and 2.0 MPa.m1/2, respectively. In vitro analysis shows that the samples have been covered by apatite cell since day one, and the density of apatite increased with immersion time in SBF. This study showed that CNT reinforcing was beneficial in producing high toughness of BCP without offsetting its bioactivity properties.

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INTRODUCTION

Biphasic calcium phosphate (BCP) ceramic materials, which are composed of different concentrations of the stable phase, hydroxyapatite (HA,$Ca_{10}(PO_4)_6(OH)_2$), and the more soluble phase, usually composed of β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$), are of special importance for humans because they represent the inorganic part of human bones and teeth and are more extensively used as bone implants [1]. A number of studies have already publicized significant advantages of implanted BCP bioceramics over pure HA or pure β -TCP [2,3]. This mixture is also considered to be a promising bone implant material due to their controlled bioactivity and balance between resorption and solubilization which guarantees the stability of the biomaterial while promoting bone ingrowth [4,5].

Zinc, an essential trace element in bone, has been attempted in the field of substituted apatites by considering all nature of human bones. It is involved in bone formation *in vitro* and *in vivo* and is potentially promising biomaterial to promote tissue growth [6,7]. Mechanical tests performed in BCP, however, show very low values of fracture toughness (0.8–1.2 $MPa.m^{1/2}$ of HA [8] compared to 2–12 $MPa.m^{1/2}$ of human cortical bone [9]. Thus this material is not suitable for heavy load-bearing applications.

Carbon nanotube (CNT) is emerging as a suitable reinforcement of compositematerial since introduced two decades ago. It has been extensively explored in recent years owing to their excellent mechanical properties. Numerous researchers have attempted to fabricate composites of HA reinforced with CNT in expectation of better mechanical properties implants. It has been a vast area of study and research lately and has showed outstanding results[10-12].

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To date, different methodologies have been reported in order to prepare HA/CNT composites [13,14]. This paper aims the development of a bulk Zn-doped BCP product reinforced with CNT to be used in biomedical applications. We have reported the synthesis of zinc-doped BCP powder elsewhere [15]. In this work, mechanical behaviour and *in vitro* analysis of BCP reinforced CNT composites was investigated.

MATERIALS AND METHODS

Synthesis of starting powder:

Zn-free BCPand Zn-doped BCP powders used to produce dense compacts were synthesized via a sol-gel technique[16]. The Zn-free BCP/CNTand Zn-doped BCP/CNT composites with 1% weight percentage of MWCNT were mixed in aqueous media. Finally, the solution was filtered and dried. After uniaxial pressing the compacted samples were sintered viaconventional pressureless sintering in the temperature range of 1000–1300^{o}C.

Each solution of BCP and CNT was firstly sonicated for approximately 30min to avoid agglomerates. This procedure was followed by adding ammonium salt of polyacrylic acid (Duramax^{TM} D-3005) as dispersant of carbon nanotubes.

Characterization:

The presence of the crystalline phase in the synthesized powder was analysed by X-ray diffraction (XRD) (Shimadzu Diffractometer, XRD-6000). The bulk density of the sintered dense samples was measured by the Archimedes principle using a standard densimeter (AlfaMirage, MD-300S). For Vickers hardness determination, the indentations were made using a pyramidal diamond indenter (Mitutoyo, MHV H-2) with an applied load of 200g. The fracture toughness (K_{Ic}) of the sintered dense samples was determined using Vickers indentation method and the KIc value was calculated using the Niihara equation. The morphology of the samples was investigated by FESEM (a JEOL JSM-6700F) and a FEI Technai T20 TEM operated at 200 kV, High Resolution.

RESULTS AND DISCUSSION

Powder characterization:

Figure 1 shows the XRD pattern of various mole percentages ofZn-doped BCP and Zn-free BCPobtained powder calcined at 900^{o}C. Sharp clear reflections proved the phase purity and crystallinity degree of the obtained powder. The figure presents peaks attributed to International Centre for Diffraction Data (ICDD), hydroxyapatite (HA, card no. 09-432) as the main phase and β-tricalciumphosphate (β-TCP, card no. 09-169) as the secondary phase.

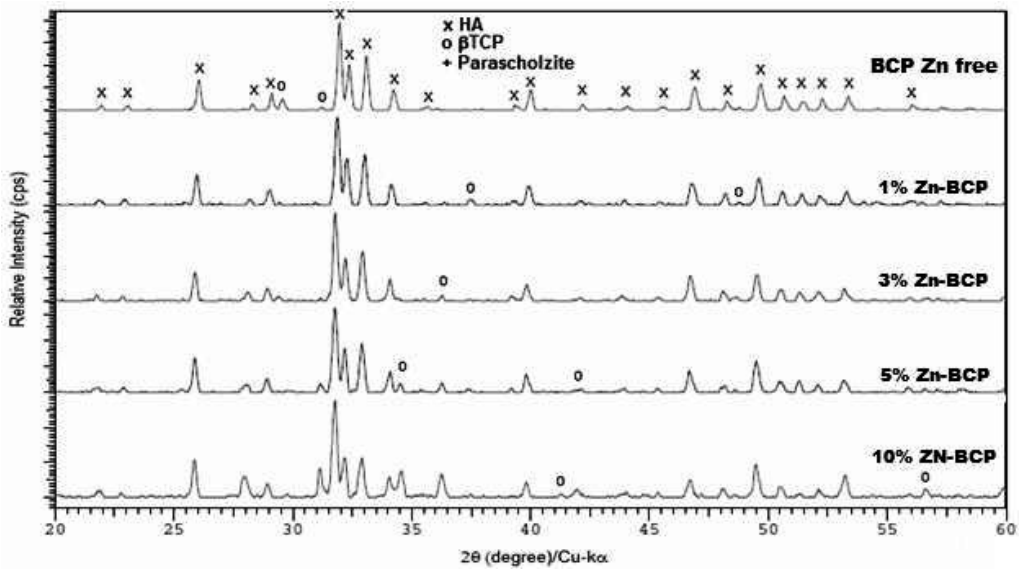

Fig. 1: Zn-doped BCP and Zn-free BCPobtained powder calcined at 900^{o}C.

It can be seen from XRD pattern that the peaks attributed to phase β-TCP increase with an increase in Zn concentration. 10mol% Zn-BCP showed the highest intensity of β-TCP peak at $2\theta = 31.32^{o}$. Results infer that the concentration of Zn which is incorporated in HA lattice, influences the thermal stability of HA. The thermal

stability of HA decreases with an increase in Zn fraction [17]. In addition, the intensity of β-TCP peaks at 2θ = 28.10°, 29.96°, 31.32°, 34.5°and 36.69° becomes more intense and narrower for 10mol% Zn-BCP. Hence, it could be deduced that in this research work β-TCP phase increase with an increase in the concentration of Zn.

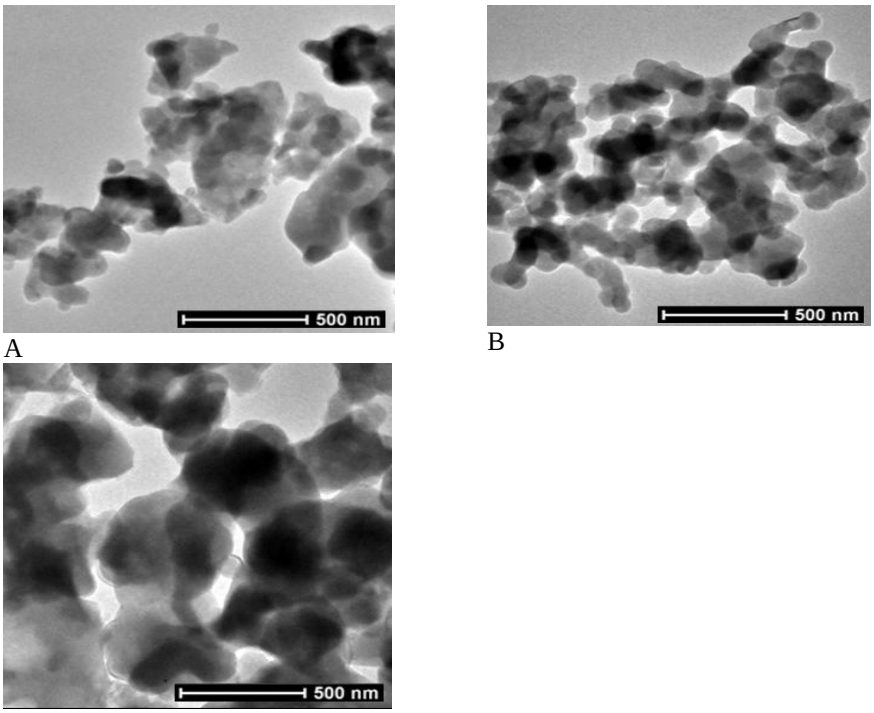

Fig. 2: TEM micrograph of Zn-doped BCP powders calcined at 900ºC: (a) Znfree-BCP (b) 5% Zn-BCP (c) 10% Zn-BCP.

The TEM image of Zn free-BCP powders is presented in Fig. 2a. It is evident of the formation of nanocrystalline powder and individual particles are globular in shape. TEM morphology of various zinc percentages are shown in Fig. 2b and c. It can be seen also that zinc concentration changes the morphology of Zn doped BCP. This led to the conclusion that the agglomeration of particle increases with an increase in Zn concentration.

Composite characterization:

Table 1 shows the relative density of various percentage moles of Zn-doped BCP/CNT composite. The maximum relative density of 97.83% was observed in the sample of 4mol% Zn-doped BCP as compared to 88.0% in Zn-free BCP.

Table 1: Density of Zn-doped BCP/CNT with various Zn concentrations.

Properties	Zn Concentration (%)			
	0	1	4	10
Apparent density (g/cm^3)	2.75	2.90	3.09	2.66
Relative density (%)	87.10	91.75	97.83	84.22

Figure 3 shows the Vickers hardness and fracture toughness (KIc) of various mole percentages of Zn-doped BCP/CNT composite fired at 1200°C. It can be seen that up to 4mol% Zn-doped BCP/CNT composite show higher Vickers hardness and fracture toughness as compared to Zn-free BCP/CNT. For Zn-free BCP/CNT Vickers hardness and fracture toughness were 3.26 GPa and 1.74 MPa.m$^{1/2}$, respectively. The maximum Vickers hardness of about 4.30 GPa was observed in the sample of 4mol% Zn-doped BCP/CNT. In contrast, 10mol% Zn-doped BCP/CNT could only be attained a maximum hardness of 3.26 GPa. It can be explained in detail via density results. The density of this sample has the lower value among the samples.

The results also show that the CNT were effective in improving the fracture toughness (KIc) of the synthesized BCP. The 4mol% Zn-doped BCP/CNT samples exhibited highest fracture toughness of 2.0 MPa.m$^{1/2}$ as compared to 1.74 MPa.m$^{1/2}$ measured for the Zn-free BCP/CNT.

The *In vitro* bioactivity analysis was evaluated using simulated body fluid (SBF) [18]. The morphology analysis of immersed sample in SBF solution is shown in Fig. 4. It can be seen that the samples have been covered by apatite cell since first day Fig. 4a-c. In addition, after 7 days of immersing in SBF the surface of

apatite layer changed through the growth of the apatite. This finding led to the deduction that the density of apatite by immersion time.

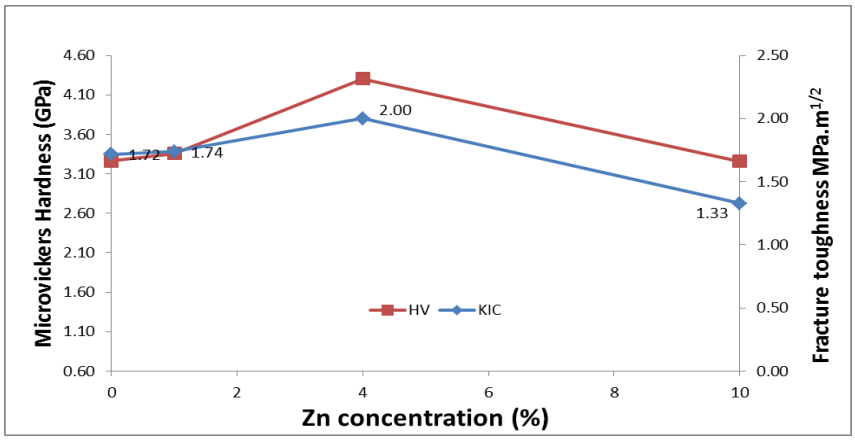

Fig. 3: The Vickers hardness and fracture toughness of various mole percentages of Zn-doped BCP/CNT composite.

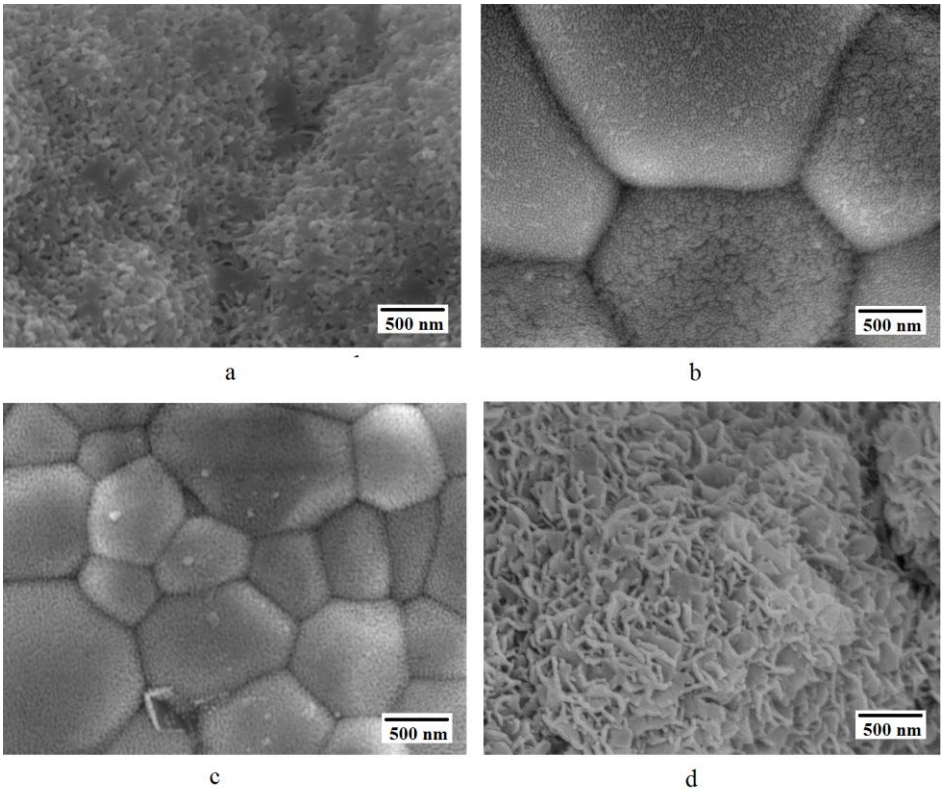

Fig. 4: The FESEM morphology after 1 day immersed in SBF solution: (a) Zn-free BCP /CNT (b) 1%Zn-doped BCP/CNT (c) 4%Zn doped BCP/CNT (d) 4%Zn-doped BCP/CNT after 7 day immersed in SBF solution

Conclusions:

In this study, Zn-free BCP/CNT and Zn-doped BCP/CNT composites have been prepared. Overall, the phase of samples was hydroxyapatite and β-tricalcium phosphate. The morphology of the powders show the formation of nanocrystalline powder and individual particles are globular in shape.The maximum Vickers hardness and fracture toughness was achieved when sintered at 1200^{o}C, with 4.30 GPa and 2.0 MPa.m$^{1/2}$, respectively. *In vitro* analysis shows that the samples have been covered by apatite cell since 1 day, and increased the density of apatite by immersion time. This study showed that CNT reinforcing was beneficial in producing high toughness of Zn doped BCP.

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