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Evaluation of biphasic calcium phosphate/nanosized 3YSZ composites as toughened materials for bone substitution

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ABSTRACT

In this research, biphasic calcium phosphate (BCP), comprising 70 wt% of beta tricalcium phosphate and 30 wt% of hydroxyapatite, was mixed with different amounts of 3 mol% yttria-stabilized zirconia (3YSZ) and sintered at 1200 °C to produce toughened bone substitutes. The fracture toughness (K_{Ic}) of the obtained bodies was determined using the indentation-strength fracture method. Scanning electron microscopy and energy dispersive X-ray spectroscopy analysis were utilized to study the microstructure of the samples. The phase composition of the samples was also determined using X-ray diffraction technique. In order to investigate the cell supporting ability of the samples, G-292 cells were cultured on them and cell morphology was evaluated after 48 h. Based on the results, the maximum fracture toughness and compressive strength values (i.e., 2.11 MPa $m^{0.5}$ and 150 MPa, respectively) were obtained for the sample containing 3 vol% of 3YSZ. The obtained fracture toughness value was approximately two times higher than that of the original BCP (1.07 MPa $m^{0.5}$) and also was comparable with that of the cortical human bone. The following mechanisms for the improved K_{Ic} of the β-tricalcium phosphate were determined: Grain bridging of 3YSZ particles during crack growth resistance, formation of microcracks on the tip of the larger cracks, absorbing crack extension energy due to the volume expansion during 3YSZ tetragonal-monoclinic transformation and crack deflection by the presence of 3YSZ particles. Also, 3YSZ additive encourages transformation of HA phase into β-TCP during sintering BCP. Finally, based on the cell studies, the samples exhibited an adequate cell attachment and a good cell spreading condition.

1. Introduction

The main reason behind the use of calcium phosphates as bone substitute and bone defect repairing agent is their chemical similarity to the mineral component of bones and teeth and their bone bonding ability [1–3]. Calcium phosphates, especially hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$) are widely used to repair and reconstruct damaged parts of the human skeleton [4]. They are biocompatible material that exhibit bioactivity in contact with living tissues [2]. Biphasic calcium phosphates (BCP) consist of an intimate mixture of hydroxyapatite (HA) and beta-tricalcium phosphate (β-TCP) of varying HA/β-TCP ratios. BCP can be obtained by sintering calcium deficient apatite above 700 °C [3]. In fact, HA is a bioactive agent, while β-TCP is a biodegradable agent in BCP composites [5]. However, the principal limitation of these materials is poor fracture toughness and their brittleness, which restricts their orthopeadic applications [6].

One of the best approaches for the improvement of mechanical properties of calcium phosphate bioceramics is combining them with tough materials [7]. An effective reinforcing agent for a ceramic-matrix material should have some requirements, including a higher strength and elastic modulus than those of the matrix, no excessive reaction with matrix and other existing phases and nearly similar coefficient of thermal expansions (CTE) to that of matrix [1]. In previous studies, several efforts have been made for increasing the fracture toughness of calcium phosphate using tough particles such as ZrO_2, Ag and Al_2O_3 [7–9].

The tetragonal zirconia which has been stabilized with 3 mol% of yttria (3YSZ) are commonly used as reinforcing agent for many ceramics, because of its excellent mechanical properties such as compressive strength and fracture toughness [7]. Toughening mechanism in ceramic composites includes: crack deflection, crack bridging by the second phase and stress-induced phase transformation, resulting in the formation of microcracks at the tips of large cracks [1]. Zirconia has a high mechanical strength and fracture toughness with optimum wear resistance and hence, is an appropriate material for orthopedic applications [10].

The fracture toughness of bioceramics can be increased based on 3YSZ phase transformation [11]. The zirconia tetragonal to

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monoclinic transformation involves volume change [12]. Consequently, the increase in energy absorption during the crack propagation originates from the stress-induced phase transformation due to the volume extension, resulting in formation of microcracks in front of the large crack [13]. This transformation happens at a temperature below 1200 °C; however, retention of the tetragonal phase is optimized by increasing density and maintaining the grain size below a critical value which is between 0.2 and 1 μm for 3YSZ [14].

Although there are some reports on the mechanical properties of zirconia/HA composites, no research has been performed to evaluate the effect of 3YSZ on phase ratio, toughness and other characteristics of BCP bioceramics. Thus, the present work aims to improve mechanical properties and phase changes of sintered BCP added with different amounts of 3YSZ nanoparticles. Since the sintering temperature plays an important role on densification and mechanical properties [15], in our pre-tests, the fracture toughness and density of various compositions sintered at 1200 °C were compared to each other. Afterward, the composite with maximum fracture toughness and density were selected for further cellular evaluations.

2. Materials and methods

2.1. Preparation and characterization of starting materials

The starting powders were commercially available precipitated hydroxyapatite (PHA, Merck Co. 102143) and polycrystalline yittria-stabilized tetragonal zirconia (3YSZ; US Research Nanomaterials, Inc. US3600). The morphology of zirconia nanoparticles was observed by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The SEM observation was performed on gold-coated particles using Tescan VEGA device at an accelerating voltage of 20 kV. For the TEM observation, 3YSZ powder was dispersed in ethanol sonicated to form a diluted suspension. Then, a few droplets were dropped on a carbon coated-copper grid. The particle morphology was observed by a GM200 PEG Philips at an accelerating voltage of 200 kV.

PHA is a calcium-deficient product, which is generally converted into a biphasic compound of β-TCP and HA during firing, through the following reaction [16]:

$$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} \leftrightarrow 1\text{–}xCa_{10}(PO_4)_6(OH)_2 + 3xCa_3(PO_4)_2 \quad (1)$$

Thus, according to our previous study [16], in order to obtain a BCP powder with β-TCP to HA phase ratio of 70–30 (in w/w), the PHA powder was heat treated at 1000 °C for 3 h.

2.2. Preparation and evaluating physical and mechanical properties of BCP/3YSZ composites

Table 1 presents different mixing ratios of the produced BCP and 3YSZ along with the code of each sample. The mixture was milled in acetone medium using a planetary ball mill with zirconia cup and balls at 220 rpm for 12 h. The solvent was evaporated by heating the suspension on a hot plate while it was stirring. After that, it was kept in an oven at 75 °C for 12 h for the complete removal of acetone. Afterwards, the powders were ground in an alumina mortar and sieved. The specimens were in two types, rectangular 20 × 5 × 4 mm bars and cylinder with 12 mm in diameter and 6 mm in height were fabricated by pressing at 60 MPa. Exclusion of any defects associated with pressing process was achieved by subsequent cold isostatic pressing (CIP) at 175 MPa. The green samples were sintered at 1200 °C for 2 h.

Table 1
The compositions of the composites comprising different amounts of BCP and 3YSZ.

Sample code	BCP (vol %)	3YSZ (vol %)
Pure BCP	100	0
BCP-1VZ	99	1
BCP-3VZ	97	3
BCP-5VZ	95	5

The compressive strength test was done on cylindrical samples with 2000 Kg_f load cell using a universal testing device (STM-20, Santam, Iran) at a crosshead speed of 0.5 mm/min^{-1} [17].

Samples were tested for K_{Ic} by indentation-strength fracture method of Chantikul et al. [18], which introduced as a modified indentation toughness technique by Cook and Lawn [19]. For this purpose, the samples were indented at the center of their fine mirror polished surface with a Vickers indenter (diamond pyramid). A contact load, P=196 N, was applied to produce a print (and hence an initial crack) on the sample surface. After that, a bending load was applied on the other side of the indented specimens to calculate three point bending strength. Bending strength (σ) was recorded using a universal testing device (STM-20, Santam, Iran) at a crosshead speed of 0.2 mm/min and span length of 16 mm. The σ value was calculated by the following formula [16]:

$$\sigma = \frac{3PL}{2bd^2} \quad (1)$$

where P was fracture load and b, d, and L were width, thickness and length of the specimen (distance between two supports), respectively.

The toughness alters as a function of crack size for ceramic composites, which is related to R-curve behavior of them. The fracture toughness value is calculated by Eqs. (2) (K field) and (3) as follows:

$$K = \psi\sigma c^{1/2} + \chi\frac{P}{c3/2} \quad (2)$$

$$\chi = \delta(E/H)^{0.5} \quad (3)$$

In Eq. (2), the first term ($\psi\sigma c^{1/2}$) is the applied mechanical field caused by the external bending stress, σ, and the second term $\left(\chi\frac{P}{c^{3/2}}\right)$ is the indentation field effect caused by load P during the Vickers indentation. The geometrical coefficient ψ is assumed to be 0.77 regarding the Chantikul et al. and indentation coefficient χ is related to the constant coefficient δ, which is assumed to be 0.016 ± 0.004. The E/H value of BCP composites is considered 0.08 [20–22]. The final crack size (c_f) was driven from the Eq. (2) at the fracture point when $dK/dc=0$. Then K_{Ic} was calculated from the Eq. (2) at the calculated $c=c_f$ ($K_{Ic}=K$ (at c_f)).

The hardness of the samples was also measured based on the Vickers indenter trace dimensions (obtained by the optical microscopy observations) using the following equation:

$$H = \frac{1.854P}{L^2} \quad (4)$$

where P was indentation load (20 Kg_f) and L was an average value of two diameters of indenter diamond print.

Density of the samples was evaluated by the Archimedes water immersion method. The porosity was calculated from the bulk density and theoretical density using the following equation:

$$P(\%) = 100\left[1 - \left(\rho_{exp}/\rho_t\right)\right] \quad (5)$$

where P is porosity in vol%, ρ_t is the theoretical density, ρ_{exp} is the value of density measured by Archimedes method.