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Fabrication and Characterization of Nanostructured Calcium Phosphate and Zirconium Dioxide Composites

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Abstract

The aim of this study is to fabricate and characterize ceramic composites made of $Ca_{10}(PO_4)_6(OH)_2$ and ZrO_2 using a simple powder pressing technique and to study the effect of addition of ZrO_2 on the biaxial flexural strength (BFS) of the ceramic composites. Various compositions of hydroxyapatite (HAp)® $Ca_{10}(PO_4)_6(OH)_2$ and zirconia powder© ZrO_2, ranging from 10 to 90 wt% ZrO_2, were prepared using a wet mixing process. Ten compacts (13.5mm×3mm) were made for each group, pressed and fired in air at sintering (firing) temperatures from 1100 to 1450^{o}C for up to 12 hrs. The bulk density, true porosity, linear shrinkage and BFS were evaluated.

The true porosity reduced and linear shrinkage increased with increasing firing temperature and amounts of zirconia, whereas the firing time had little effect. The highest mean value achieved for the BFS was 269 MPa (±20) for a composition of 70% ZrO_2 and 30% HAp fired at 1450^{o}C for 6 hrs, however with the hydroxyapatite (HAp) decomposed to α-TCP as reported earlier [1].

We conclude that firing temperature and composition affect densification behaviour of calcium phosphate/ZrO_2 ceramic composites. The BFS increases with a reduction of porosity and increases with both firing temperature and additions of ZrO_2. It was noted that there is considerable scope for improvement in the BFS values by reducing the porosity of these ceramics composite. Further work is needed to examine the crystals structure and to elucidate the microstructural features of the composites.

Keywords: Fabrication, Characterization, Composites, Powder Pressing Technique, Biaxial Flexural Strength, True Porosity.

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Introduction

Hydroxyapatite (HAp) with the chemical composition $Ca_{10}(PO_4)_6(OH)_2$ has been extensively study as a bone substitute. It shows an excellent biocompatibility when implanted in either soft tissue [2-4], or hard tissue [5, 6-8] and can form strong and intimate bond with bone [4,6,7]. Driskell *et al.* [9] was the first to report that a chemical bond exists between bone and HAp. HAp, when fired at high temperatures of up to 1250°C, was initially believed to be non-resorbable [2]. However, it is currently generally accepted that degradation of HAp can occur to a certain extent [5,10]. LeGeros, *et al.* [11] reported that the bioactivity of HAp may be related to its dissolution rate.

HAp is mechanically weak and unsuitable for use in stress bearing areas. Two approaches have been explored to overcome this problem [12,13].

One of the most promising applications of calcium phosphate technology revolves around the use of HAp coatings on conventional metallic prostheses. Among the advantages of this approach is the potential for stronger, more permanent fixation of the metal implant directly to surrounding bone via HAp bone-bonding and the elimination of leaching of metallic trace elements into adjacent tissues. In the case of major orthopaedic appliances such as total hips and knees, a strongly adherent HAp coating on the metallic devices could obviate the need for methyl methacrylate bone cement, which has proved to be the limiting factor in long-term survival of such devices. However, all commonly used coating techniques depend on mechanical adhesion (rather than a chemical bond) to the underlying metal which makes this metal-HAp interface the weakest point of the system [14,15] Ducheyne *et al.* [12] used HAp as surface layer on titanium implants, but this approach has several problems that include separation of the coating layer from the underlying bioinert matrix and the coating process can reduce the strength of the bioinert materials [13]. In vivo studies [16,17] have assessed bony adaptation to HAp-coated and non-coated pure titanium control implants. One study demonstrated an increased amount of direct bone to implant contact with coated specimen at six weeks [17]. Sharp edges or deep threads observed on the base metal also reduce the adherence properties of these ceramics. Another concern is the dissolution of improperly applied coatings with time, and consequences that both bond strength and coating integrity will be affected [14,16-18].

The second approach is to produce HAp/ ceramic composite with better mechanical properties with HAp [12,19] such as ZrO_2-HAp, Ti-HAp, Al_2O_3-HAp composites. The even distribution of the apatite phase as islets in a strong matrix may contribute to mineralization and direct bone apposition onto this type of ceramic composite [13,19,20].

The objective of this study concerned with structural ceramics is the generation of materials having high reliability. To achieve this objective, there are two fundamentally different approaches: flaw control and toughening. The flaw control approach accepts the brittleness of the material and attempts to control the large extremes of processing flaws. The toughening approach attempts to create microstructures that impart sufficient fracture resistance so that the strength becomes insensitive to the size of flaws. The former has been the subject of considerable research that identifies the most detrimental processing flaws, as well as the processing step responsible for those flaws [21-23]. The latter has emerged more recently, and has the obvious advantage that appreciable processing and post-processing damage can be tolerated without compromising the structural reliability [23-25].

Composite materials which combine the properties of a ceramic matrix and ceramic reinforcement or aggregate phase, otherwise known as ceramic matrix composites, are the subject of intense research interest. With careful processing improved strength and toughness can be obtained when compared to unreinforced ceramics. Composite such as zirconia toughened Al_2O_3 (ZTA), TiC-Al_2O_3 and SiC-Al_2O_3 are currently used as wear resistant bearings and cutting tools. A variety of ceramic composites are been explored for medical applications e.g. ZrO_2-HAp, Ti-HAp, Al_2O_3-HAp composites.

Molecularly designed composite materials that mimic the structure and properties of bone offer the greatest potential for solving the problems of interfacial stability and stress shielding of load-bearing prostheses. This is because the modulus of elasticity and fracture toughness of a composite is a function of many variables which can be controlled during processing. Various combinations of low elastic modulus bioactive materials, and higher elastic modulus bio-inert materials, can yield composites with properties that are similar to those of bone. This type of composite should eliminate stress shielding of bone because there is no mismatch in elastic modulus across the implant-bone interface. Use of a dispersed phase that has a bioactive property can ensure that rapid bone bonding occurs.

In a study perfomed by Jianguo *et al.* [26], a range of high-strength hydroxyapatite composites (HAp/Oxide of Alumina, Titania or Zirconia) as well as pure hydroxyapatite, alumina, titania and zirconia were densified by hot isostatic pressing. The mechanical evaluation showed that the strength of the composite materials was 3-8 times higher than that of pure hydroxyapatite and close to that of the corresponding pure oxide. These ceramics were implanted in the femora of 16 rabbits for three months. Eight rabbits were sacrificed for histological evaluation and the others used for push-out test in order to study the bond strength between bone and ceramic implants. Histological evaluation under the light microscope showed direct contact between bone and ceramics for all ceramic materials studied except for alumina. The measured bond strengths in this experiment increased in the following order: alumina, titania, zirconia/hydroxyapatite, alumina/hydroxyapatite, titania/hydroxyapatite, hydroxyapatite. However, the authors did not give the firing temperature to produce the fired ceramics, neither did they characterise their materials to show if there was decomposition of HAp or interaction between HAp and other oxide and so it is not clear if the processed materials were genuinely composites of the two starting materials or their reaction product.

Kasuga, *et al.* [27] have reported on a glass-ceramic (apatite/wollastonite) toughened with zirconia which were prepared for widespread prosthetic applications. The strength of the composite increased with increasing zirconia content. This bioceramic exhibited extremely high bending strength (400-1000 MPa) for 30-80 vol.% ZrO_2. The bioactivity of these zirconia toughened glass-ceramic composites was evaluated by their bond strength to living bones, and it was found that the bond strength of composite containing 30 vol.% zirconia was as high as that of the glass-ceramic.

Lately investigators have demonstrated that the mechanical reliability of HAp can be improved by reinforcing HAp with Al_2O_3 [28-33]. The main problems in producing dense composites in this system are connected with the big difference in firing temperature of the components, the enhanced tendency of HAp to decompose during firing and the consequent interaction between HAp and reinforced phase. An attempt at producing an HAp/Al_2O_3 composite [34] fired at 1400^{o}C in air, resulted in the formation of calcium aluminates, due to decomposition of hydroxyapatite into TCP and CaO with H_2O vapour. CaO then reacted with alumina to form calcium aluminates.

Several researcher have reported [35,36-39] on hydroxyapatite-zirconia composites with different volume ratio of zirconia particles. Most of these works reflect the difficulties of retaining the HAp and ZrO_2 phases in the composites due to difference in densification temperature (e.g. HAp start to densify at 1250^{o}C, whereas ZrO_2 start to densify at 1400^{o}C), and decomposition of HAp at 1400^{o}C into TCP. As a consequence the desirable initial phases cannot be preserved in the composites unless expensive high technology processing at temperatures as low as 1250^{o}C is used.

Suda *et al.* [35] have produced composites contained either 1.6 or 50% of ZrO_2 by volume addition to HAp, using cold isostatic pressure (CIP), then fired at 1300-1450°C in air atmosphere for 1 hr. Although the bending strength of their composite is 220-270 MPa, and the fracture toughness is 3.6-4.5 $MPa.m^{1/2}$, they did not characterise their materials to show if there is decomposition of HAp or interaction between HAp and ZrO_2. Since even high purity HAp decomposes into tri-calcium phosphate (TCP) at 1250°C [40], and the fact that they fired their materials at firing temperatures higher than 1250°C, it has to be concluded that the materials obtained could not possibly be HAp/ZrO_2 composites.

Takagi *et al.* [13] produced HAp/ZrO_2 composites using hot isostatic pressing (HIP) at 800-1150°C at 100 MPa for 2 hr. No phase change was found in zirconia nor in the HAp phase. The strength and the toughness achieved were respectively 190 MPa and 2.3 $MPa.m^{1/2}$. These values were approximately 20% and 100% higher than the corresponding value for hydroxyapatite ceramics without zirconia. Li *et al.* [20] also used HIPing (1225°C at 160 MPa for 1 hr) to produce HAp/ZrO_2 composite that has excellent fatigue resistance in addition to high strength, but they did not characterised the fired composite.

The objective of this study is to develop a bioactive, high strength and toughness calcium phosphate/ ZrO_2 composite, which can be used in load bearing applications.

Materials and Methods

Hydroxyapatite (HAp) $Ca_{10}(PO_4)_6(OH)_2$ and zirconia powder ZrO_2 powders were used in this study, supplied by Plasma Biotal Ltd, Tidswell, and Unitec Ceramics, Stafford, UK respectively. The particles sizes of both powders were determined using particle size analyser (Coulter LS 130) which employs a laser diffraction method.

The bulk density, true porosity, linear shrinkage and BFS were determined for the fired samples. The bulk density values were calculated using the following equation:

$$Bulk\ \ Density = \frac{Weight\ (g)}{Bulk\ \ Volume\ (cm^3)} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Hence, *Bulk Volume* = $r^2 h\pi$, where r and h are the compact's radius and height respectively.

The % theoretical density values were calculated using the bulk density of the compacts and the theoretical density value for HAp and zirconia of 3.156 and 6.05 gcm^{-3} respectively [40,41,42].

$$Theoretical\ Density\ (\%) = \frac{Bulk\ \ Density\ (gcm^{-3})}{Theoretical\ Density\ (gcm^{-3})} \times 100 \ldots\ldots\ldots\ldots(2)$$

Also, the true porosity values were calculated using the following formula:

$$True\ Porosity (\%) = 1 - \left(\frac{Bulk\ \ Density\ (gcm^{-3})}{Theoretical\ Density\ (gcm^{-3})}\right) \times 100 \ldots\ldots\ldots\ldots\ldots(3)$$

The linear shrinkage values of the fired compacts were determined by measuring the initial and the fired diameters of each sample as follow:

$$Linear\ Shrinkage (\%) = \frac{Di - Df}{Di} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where, D_i and D_f are the initial and the fired diameter of the compact.

The BFS for a range of firing schedules of each HAp and ZrO_2 powder was determined for 10 test-pieces. The surfaces of the test-pieces were made flat by grinding with 600 grit SiC paper to avoid an uneven load. Each test-piece was placed on an annular knife edge of 9 mm diameter and then loaded in a universal testing machine with a cross-head speed of 0.5mm/min (Lloyd M5K). The compacts were loaded to fracture and the maximum load was recorded. The BFS was calculated using the following formula [43]:

$$\sigma_f = \frac{p}{h^2}\{0.606\ln(a/h)+1.13\} \quad \text{……………………………………(5)}$$

where σ_f is the BFS, p is the load to fracture, a is the radius of the knife-edge support and h is the sample thickness.

Fracture toughness values of hot pressed HAp, 30:70 vol.% HAp:ZrO_2 composite and ZrO_2 samples were determined.

Results

Characterization of the Starting Powders

The particles size of the starting powders were evaluated using particle size analyser type Coulter LS 130, this instrument employs a laser diffraction technique. The mean particle size of ZrO_2 sample-1 (coded-U) was 0.5μm and ZrO_2 sample-2 (coded-M) was 1.6μm. Both powders were agglomerated structures. The main characteristics properties of the starting powders of HAp have been described and reported earlier [1].

Sintering Behaviour of the Fired Samples

The sintering behaviour of the fired HAp samples for the theoretical density, linear firing shrinkage and the BFS have been reported previously by Shareef *et al.* [1], whereas for the fired samples prepared from ZrO_2 sample coded-U and ZrO_2 sample coded-M used in this study are presented in Figs. 1, 2, and 3. These were found increase with increasing the sintering temperature.

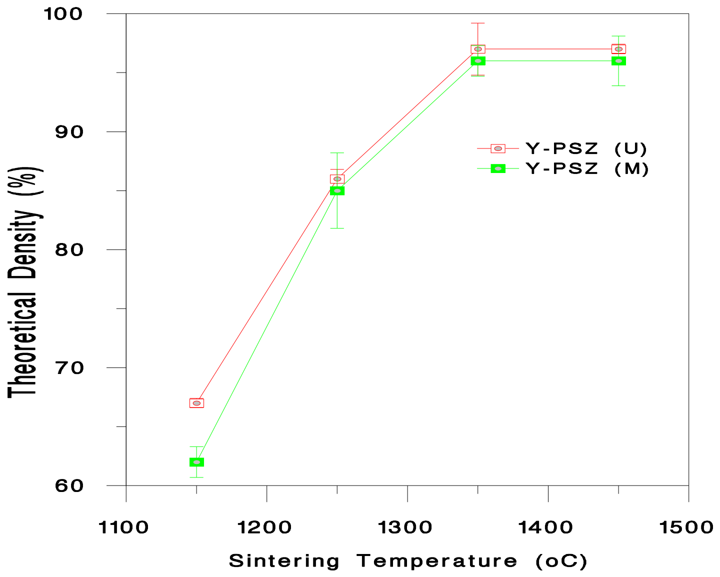

Figure 1: The effect of sintering temperature on the % theoretical density of ZrO_2-U and ZrO_2-M samples, fired for 6 hr an in air atmosphere (Y-PSZ is yttrium partially stabilised zirconia).

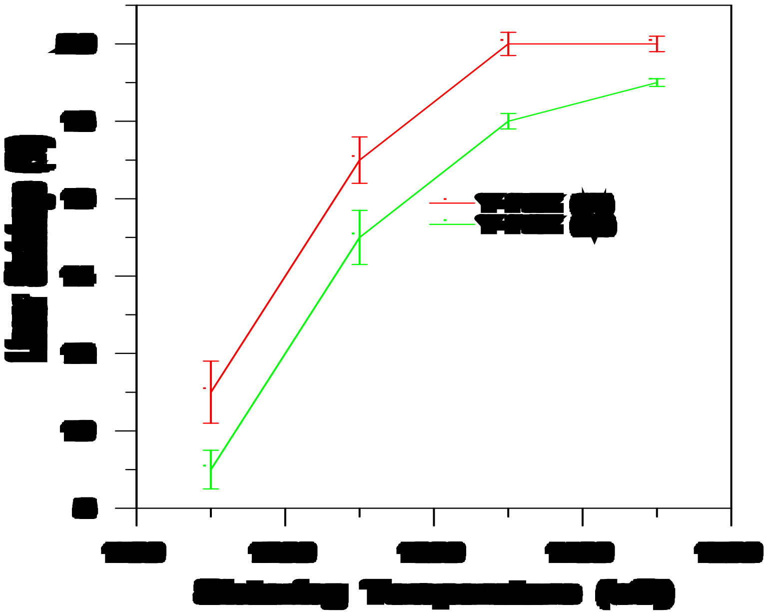

Figure 2: The effect of sintering temperature on the % linear shrinkage of ZrO_2-U and ZrO_2-M samples, fired for 6 hr in an air atmosphere (Y-PSZ is yttrium partially stabilised zirconia).

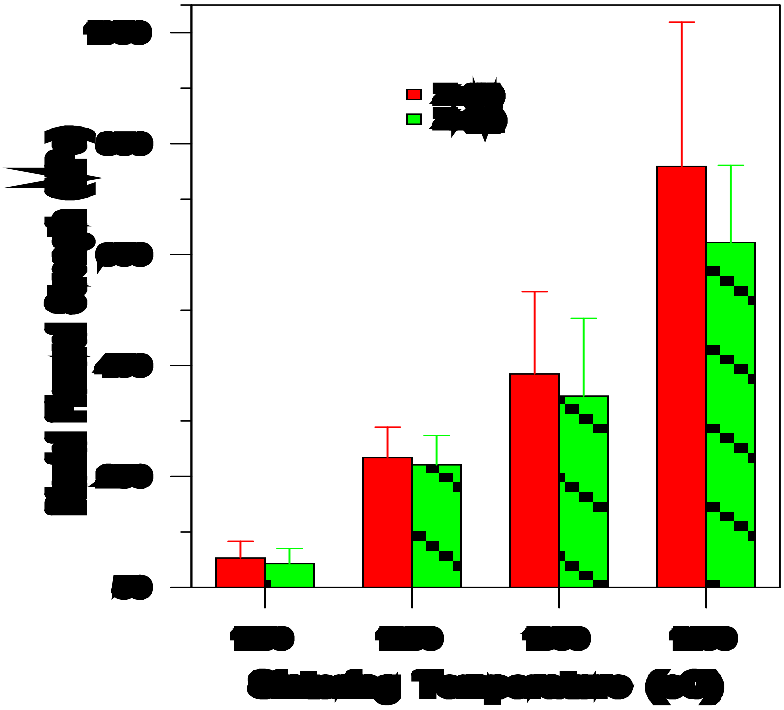

Figure 3: The effect of sintering temperature on the BFS of ZrO_2-U and ZrO_2-M samples, fired for 6 hr in an air atmosphere.

The sintering behaviour of the fired HAp/ ZrO_2 composite for the theoretical density, linear firing shrinkage and the BFS values were plotted against sintering temperature, time and addition of ZrO_2 as shown in Figs. 4, 5 and 6. These were found increase with increasing firing temperature, time and addition of ZrO_2. As shown in Fig. 6, the highest mean value achieved for the BFS was 269 ±20 MPa for a composition of 70% ZrO_2-U, fired at 1450°C for 6 hr, because the densification process reached to the highest fired density and resulting lower porosity values as shown in Table 1. However, with the hydroxyapatite (HAp) decomposed to α-TCP as reported previously [1]. On the other hand the fracture toughness values for the hot pressed samples prepared from HAp, HAp/ ZrO_2 composite and ZrO_2 are plotted against the materials used as shown in Fig. 7. Also, the main values of the BFS, fracture toughness and the fired theoretical density are shown in Table 2.

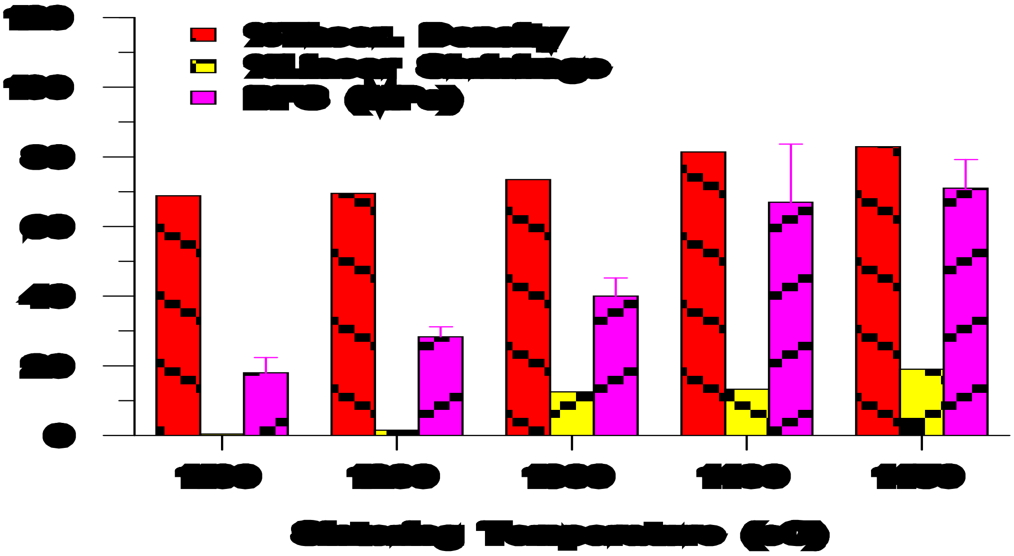

Figure 4: Theoretical density, Linear shrinkage and BFS plotted as a function of sintering temperature for samples prepared from composite of 45:55 vol.% HAp:ZrO_2-U fired for 6 hr.

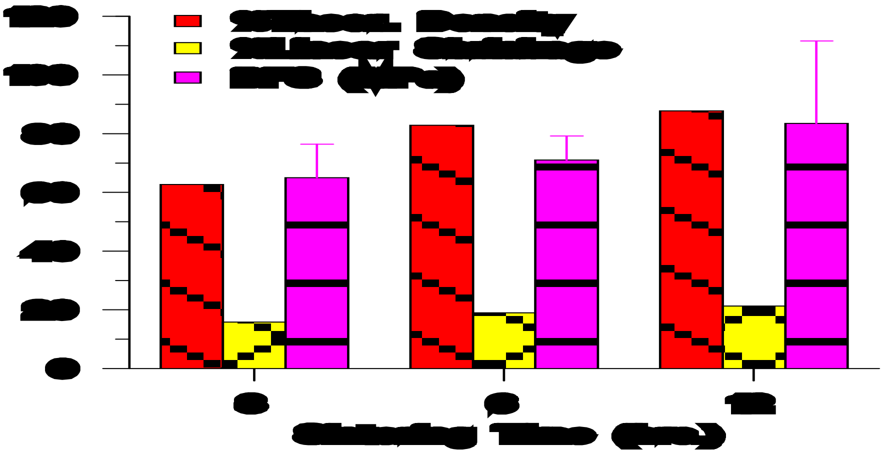

Figure 5: Theoretical density, linear shrinkage and BFS plotted as a function of sintering time for samples prepared from composite of 45:55 vol.% HAp:ZrO_{2}-U composite fired at 1450°C.

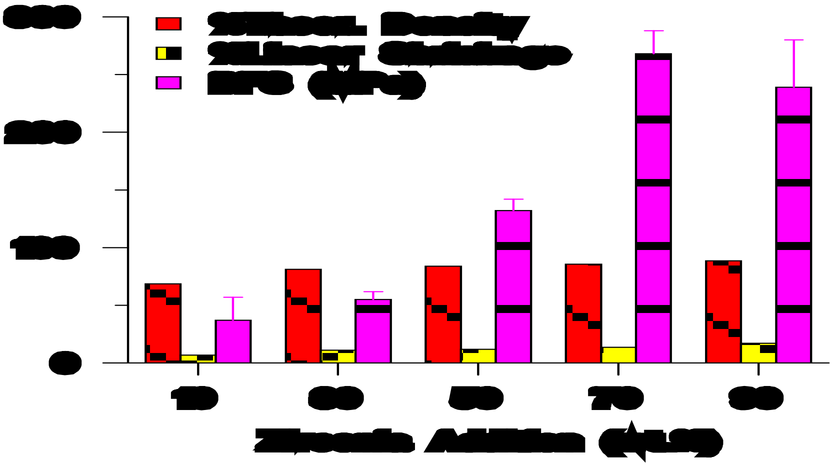

Figure 6: Theoretical density, linear shrinkage and BFS plotted as a function of zirconia addition, fired at 1450°C for 6 hr.

Table 1: BFS and % theoretical density data of composite prepared from composition of 30:70 vol.% HAp:ZrO_2-U.

Parameters	**HAp/ ZrO_2-U**	**HAp/ ZrO_2-M**
BFS (MPa)	269 ± 20	176 ± 10
% Theoretical Density	95 ± 0.5	85 ± 0.8
% True Porosity	5	15

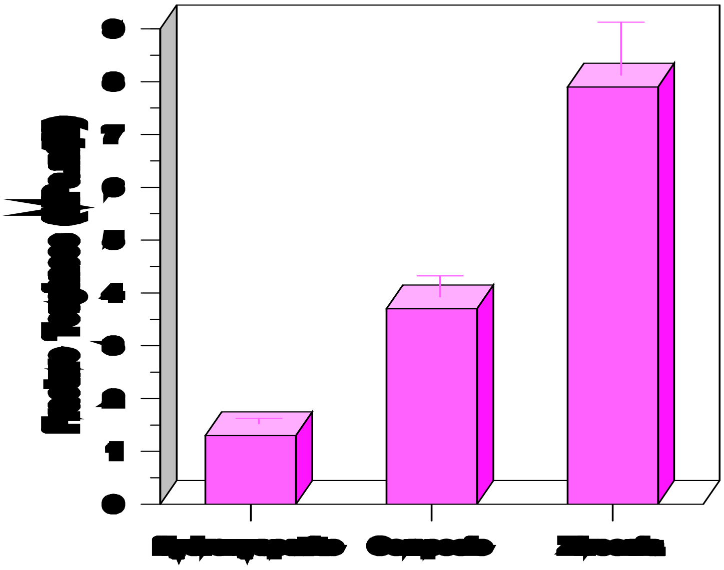

Figure 7: Fracture toughness of hot pressed HAp, 30:70 vol.% HAp:ZrO_2-U composite and ZrO_2-U samples.

Table 2: The main values of BFS, fractures toughness and the fired theoretical density of hot pressed HAp, HAp:ZrO_2-U composite and ZrO_2-U ceramics.

Parameter	**HAp**	**30:70 vol.% (HAp: ZrO_2)**	**ZrO_2**
BFS (MPa)	142±17	269±19	1213±223
Fracture Toughness (MPa.$m^{1/2}$)	1.3±0.1	3.8±0.4	8.2±1.0
%Theoretical Density	94±4	95±0.5	99±0.8

Discussion

It has been found that, by increasing the sintering temperature, time and addition of ZrO_2, the theoretical density and linear shrinkage values were increased for the HAp/ ZrO_2 composites. This cause an increase in the BFS values because the densification process increased with increasing these factors (Figs. 1, 2 and 3). The same observation has been found by Takagi *et al.* [13], which is stated that the densification behaviour of HAp/ ZrO_2 composite increased with increasing firing temperature and the amount of zirconia content. The development of HAp toughened materials by dispersed zirconia particles has been found difficult as reported by Evans [22,23] and Wu *et al.* [19]. One major obstacle has been found the reaction between the matrix and dispersed particles during the sintering process. Calcium which is the major constituent of HAp, diffuse into ZrO_2 and change it to stable cubic phase, for which a transformation toughening mechanism is not expected to occur as reported by Takagi *et al.* [13]. To avoid the difficulty associated with the diffusion, the temperature for densification has to be minimised. However, this is difficult because the composites generally have inferior sintering characteristics, and require high temperature for densification.

Takagi *et al.* [13] achieving considerable reduction of densification temperature in a composite ceramics containing ZrO_2 particles dispersed in HAp using combined application of a colloidal pressing technique and densification by hot isostatic pressing.

The calcium phosphate/ZrO_2 composite obtained in this study was contained approximately 5% porosity. Further work is needed by using a hot pressing technique and reducing the particles size to enhance the uniformity of the microstructures of the composite. This will eliminate the porosity on one hand and to reduce the sintering temperature on the other hand to level which keeps HAp thermally stable at certain sintering temperatures as reported earlier by Shareef *et al.* [1]. Also, further work is required to elucidate the crystal structures and their morphology and to examine the microstructural changes during heat treatments.

Conclusions

1. Sintering temperature and addition of ZrO_2 were affected the densification behaviour of HAp/ ZrO_2 composite, whereas the firing time had little effect.
2. The BFS values were increased with an increase both sintering temperature and additions of zirconia. Also, there is considerable scope for improvement in the BFS and fracture toughness values by reducing the porosity and the particles size of these composites.
3. The nanostructured composite material of this research is expected to have a potential use in different medical applications in the society; therefore, it is required to be developed by optimizing the mechanical properties and retains its biocompatibility.

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