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Sintering effects on mechanical properties of glass-reinforced hydroxyapatite composites

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Abstract

The improvement of mechanical properties of hydroxyapatite (HA) with reinforcement of two (45.5 wt.% P_2O_5, 54.5 wt.% CaO) and three-oxide (45 wt.% P_2O_5, 28 wt.% CaO, 27 wt.% Na_2O) glasses with different sintering temperatures is studied. Although HA shows great biocompatibility with the human body, its applications are limited to non load-bearing areas and coatings due to its low mechanical properties. These mechanical properties can be improved substantially with addition of glass ceramics by sintering. In this study, naturally produced HA from human teeth is sintered with varying addition of two and three-oxide glass ceramics. The microhardness measurements, the density and the compression tests are performed in order to find the optimum sintering temperature. Finally average hardness value of 285 ± 19 HV, average density of 2.79 ± 0.05 g cm^{-3} and compressive strength value of $\sigma_{avr} = 67 \pm 17$ MPa have been achieved by sintering at 1200 °C with the addition of 10 wt.% two oxide glass into the HA. Results are implying that 10 wt.% of glass addition for HA composites is the maximum limit for such composites. Observations are supporting the idea that sodium free glasses could be better conciliated with the HA structure at high temperatures.

Keywords: A. Sintering; B. Composites; D. Glass ceramics; Hydroxyapatite

1. Introduction

Bioactive ceramics, such as bioglass and dense hydroxyapatite (HA), have been developed over the last two decades. Their accomplishments in the field of biomedical applications, especially in prosthetic applications, have attracted wide attention [1]. Calcium phosphate ceramics, especially HA, are currently used as biomaterials for many applications in both dentistry and orthopedics, because they form a real bond with the surrounding bone tissue when implanted. Nevertheless, due to the poor mechanical properties of bulk HA ceramics, such materials cannot be used as implant devices for load-bearing applications [2]. On the other hand it is well known that the incorporation of a ceramic reinforcement (i.e. fibres, whiskers, platelets or particles) in a ceramic matrix improves the mechanical properties. In return, compared with the monolitic matrix behavior, the presence of a reinforcement opposes the sintering process [3]. Sintering is the term used to describe the consolidation of the product during firing. Consolidation implies that within the product, particles have joined together into strong aggregate. The term sintering is often interpreted to imply that shrinkage and densification have occurred. Sintered HA implants are observed to develop cracks. Thus, an optimization of the strength and microstructure of HA implants by a suitable choice of sintering parameters are needed. Glasses within the P_2O_5–CaO–Na_2O system possess enormous potential as biomaterials, because their compositions are similar to that of the inorganic constituent of the mineral part of bone [4]. All constituents of bioactive glasses could potentially be used as additives to HA ceramics to improve properties of the HA ceramic [5]. In experimental studies related to the reinforcement of HA, it is observed that glass-reinforced HA composites exhibit greater biological activities than commercial HA [6]. The purpose of this research is to determine variation of mechanical properties of

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biologically derived HA–glass composites depending on reinforcement content and sintering temperature.

2. Materials and experimental procedure

2.1. Production of HA

The HA material used in this study was derived from freshly-extracted human teeth. The teeth were irrigated with tap-water [7] and soaked in a 1 wt.% concentration of antiseptic solution to prevent bad odor and contamination of various infectious diseases. Subsequently the teeth were reirrigated and deproteinized in an alkali solution (1% concentration of sodium hypochloride). Thereafter samples were reirrigated with tap-water again. All samples were heated to 850 °C with a heating rate of 5 °C min^{-1} and kept at that temperature for 5–6 h. Easily separation of the dentine and enamel matter have been observed at that temperature, and approximately 60% of the material was dentine and 40% enamel. Enamel and dentine parts were subjected to grinding with a blade grinder for 30 s. Following this resulting samples were then sieved and only dentine based HA particles with a particle size of 106–150 μm were used in this research [7].

2.2. Preparation of bioglass compositions

Phosphate-based glasses with the chemical compositions listed in Table 1, were prepared from reagent grade chemicals P_2O_5, $CaCO_3$ and Na_2CO_3 (Merck Ltd.) as described by Santos et al. [4]. Chemicals were placed in a platinum crucible and heated at 1200 °C for 3 h. Once the glass was poured, it was milled to a powder-type particle in a porcelain ball mill for 24 h. Acetone (Merck Ltd.) and HA were wet milled together further for 24 h, and then HA and glass compositions were ball milled with acetone together with a varying amount of reinforcement content.

2.3. Sample preparation

A die was designed to prepare samples with a diameter of 11 mm according to British Standard for compression tests no. 7253. The powders were weighed to total 3.25 g. portions. The prepared portions were uniaxially pressed at 350 MPa between hardened steel dies (die height 5 mm). In this study no lubricant like polyvinylalcohol was not used. All materials were kept out for a couple days in normal atmospheric conditions and kept slightly humid. It was observed before that sintered powders would not compact together due to the lack of humidity [8]. Pressed samples were sintered in an open atmospheric oven up to temperatures 1200 °C, and 1300 °C with a heating rate of 4 °C per minute.

Table 1
Chemical composition (mol%) of phosphate-based glasses

Glass addition	P_2O_5	CaO	Na_2CO_3
2 Oxide	45.5	54.5	–
3 Oxide	45.0	28.0	27.0

2.4. Mechanical testing

The density of sintered samples was determined by the Archimedes method. Vickers hardness values were obtained using a Shimadzu microhardness testing machine with 100 g load. Compression test according to British Standard 7253 were carried out with a universal test machine (Instron 1195) at a cross head speed of 2 mm min^{-1}. All tests were performed to at least 10 specimens and their averages were taken as the main measurement.

3. Results

Density, compression and microhardness tests results for HA–glass composites are listed in Tables 2 and 3. Results indicated that HA–glass composites have significantly higher density values compared to HA sintered bodies reported previously [9]. In that study densities of sintered pure HA were found 2.59 and 2.48 g/cm^3 at 1200–1300 °C respectively, whereas densities of HA-glass composites varied about from 2.81–2.77 g/cm^3 depending on glass type reinforcement and sintering temperature (Tables 2–3). Experimental data are strongly supporting the idea of existence a very good

Table 2
Sintering results of HA and two-oxide glass composites in two sintering temperatures

Temperature (°C) and (%)	ρ_{avr} (gr cm^{-3})	σ_{avr} (MPa)	$Hardness_{avr}$ (HV)
1200 (5)	2.81±0.12	64±27	250±19
1200 (10)	2.79±0.05	67±17	285±19
1300 (5)	2.77±0.05	39±9	238±26
1300 (10)	2.76±0.05	53±11	279±12

Table 3
Results of HA and three-oxide glass composites in two sintering temperatures

Temperature (°C) and (%)	ρ_{avr} (gr cm^{-3})	σ_{avr} (MPa)	$Hardness_{avr}$ (HV)
1200 (5)	2.79±0.05	36±11	222±23
1200 (10)	2.76±0.11	40±21	259±15
1300 (5)	2.79±0.04	55±14	358±18
1300 (10)	2.79±0.14	39±12	301±8

wettening between HA particles and glass reinforcement. Sintering of HA is complicated by the fact that HA is hydrated phase that decomposes to anhydrous calcium phosphates such as TCP at ~1200–1450 °C. Decomposition results from dehydroxylation beyond a critical point. For temperatures below the critical point (1300 °C), the HA crystal structure is retained despite dehydroxylation, and the HA rehydrates on cooling. If the critical point is exceeded, complete and irreversible dehydroxylation occurs, resulting in collapse of the HA structure and decomposition. Significant reversible dehydroxylation generally occurs above ~800 °C. After the critical point α-TCP and β-TCP are often formed. In particular the molecular volume increase that occur in the β-TCP → α-TCP transformation seem to be the most deleterious phenomenon for mechanical properties [10]. Fig. 1(a) and (b) reveal that increasing sintering temperature decreases density of composites. A decrease in density could be attributed to the initation of β-TCP to α-TCP transformation at that temperature range.

Compression test results of HA/two-oxide glass composites were showed substantially higher strength values compared to HA sintered bodies. While strengths have been observed 56 and 56 MPa for HA bodies sintered at 1200 and 1300 °C respectively, they were obtained interesting values of 64 MPa, 67 MPa at 1200 °C and 39 MPa, 53 MPa at 1300 °C as seen in Table 2. It is observed from the table that the higher the sintering temperature is the lower the compression strength. On the other hand three oxide reinforced HA composites showed lower strength values compared to two oxide reinforced composites. Compression strength values of three oxide reinforced HA system are lower than that of two oxide–HA composites with respect to corresponding sintering temperature with an exception corresponding to 5 wt.% three oxide reinforced composite sintered at 1300 °C. The reason of high standard deviation values also can be attributed to brittleness character of HA.

Variations of compressive strength depending on sintering temperature and reinforcement content are shown in Fig. 2a and b. It can be observed that increasing reinforcement content increases compressive strength at constant temperature but the higher the sintering temperature is the lower the compressive strength for two oxide containing composites (Fig. 2a). On the other hand this fact is reverse for three oxide composite, the lower sintering temperature the lower compressive strength. Increasing the temperature resulted in higher compressive strength for 5 wt.% reinforcement but for a higher reinforcement content, the strength remains low whatever the sintering temperature. The reason of such an effect will be discussed in following section.

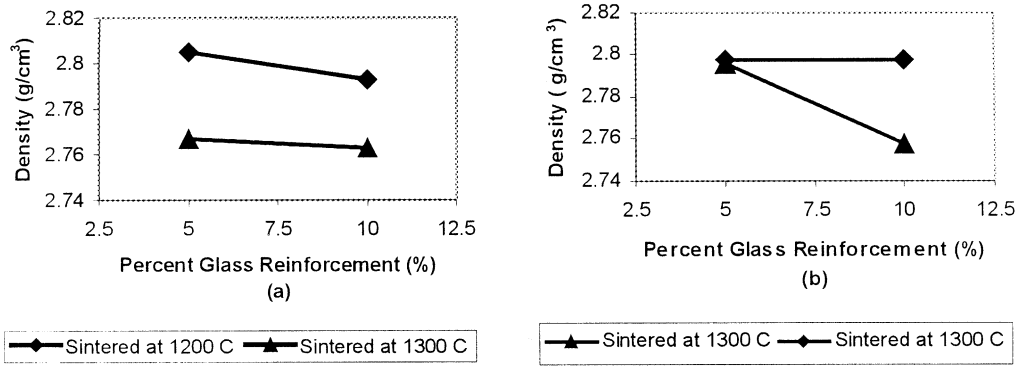

Fig. 1. Sinterability with (a) two-oxide and (b) three-oxide glass reinforced HA composites at two temperatures.

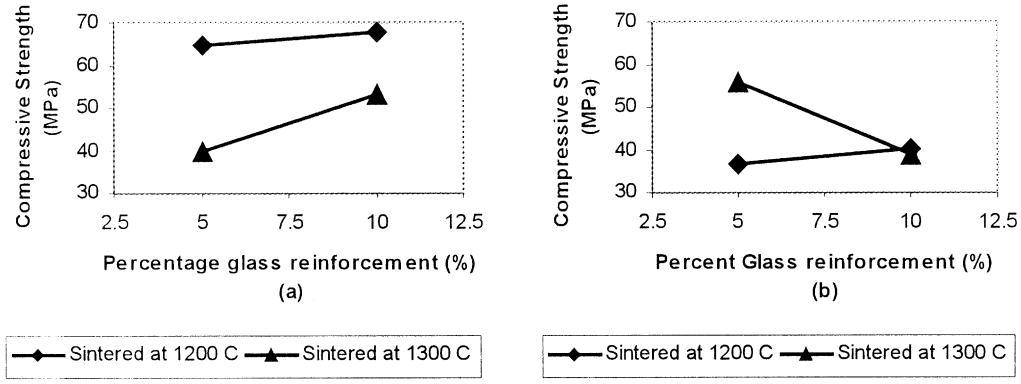

Fig. 2. Variations in compressive strength in (a) two-oxide and (b) three-oxide glass reinforced HA composites at two sintering temperatures.

4. Discussion

Santos et al. have reported that the mechanical properties of HA can be dramatically increased by the incorporation of a glassy phase during its sintering process. The glasses chosen were phosphate-based glasses closely related to the composition of HA. A strong chemical bond is developed between HA and the phosphate-based glasses at high temperatures. The liquid phosphate phase acted on the solid HA particles to reduce interfacial energy and promote the kinetics of the sintering process by a faster atomic diffusion than the concurrent solid state process of single HA. As a result of this chemical bonding, TCP phases were formed and the porosity was eliminated. The presence of a highly soluble tricalcium phosphate phase, β-TCP, formed from the reaction between bioglass and the HA matrix during liquid phase sintering process, induces a much faster Ca, P formation than HA. These statements are all in good agreement with our experimental results. Good wettening between two phases and porosity elimination resulted in increased density and hardness values (Tables 2 and 3) as compared to HA sintered bodies.

In experimental studies, short sintering time and limited glass addition such as 2.5–5 wt.%, were used to control phase transformation between two phases [11,4,12], and observed that greater amount of phase transformation occurred with the addition of 5 wt.% $CaO–P_2O_5$ but there were no research available related to two oxide or three oxide addition into HA up to the level of 10 wt.% in the literature. It was observed that the use of $CaO–P_2O_5$ type glass for the production of reinforced HA was significantly benefit to the stabilization and the tailoring of high strength values of the HA (35–88 MPa) [13]. Another crucial point is the behavior of Na containing glass compositions in HA composites. It was proposed in a study that Na including glass system was not stable above 700 °C. The sodium ions diffused from the glass phase into the HA structure which then transformed into rhenanite. The diffusion process was not extremely fast and with sufficiently short reaction times that the sodium ions had not reached the centres of the HA particles [14]. Data indicate that compressive strengths for two-oxide glass reinforced HA composites are very good for 5 and 10 wt.% addition at 1200 °C but these values are decreased at 1300 °C. It should also be noted that compressive strength and hardness values of samples containing 10 wt.% two oxide glass is better than for 5 wt.% reinforced composites whereas this fact is reverse with three-oxide glass system of which the hardness is lower for 10 wt.% glass reinforcement than for 5 wt.%. Lower values of hardness for three oxide system are indicating that sodium free two oxide systems are superior to sodium containing glass systems. All these results and lower hardness values obtained for three-oxide systems can be attributed to sodium effect on lattice structure. These facts are in agreement with Kangasniemi et al. findings [14].

5. Conclusions

Optimum mechanical properties of HA–glass composites can be achieved by sintering at 1200 °C with the addition of 10 wt.% two oxide glass into the HA. Experimental data are implying that 10 wt.% of glass addition for HA composites is the maximum limit for such composites. Observations are supporting the idea that sodium free glasses could be better conciliated with the HA structure at high temperatures.

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