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Short communication

Processing and characterization of bioglass reinforced hydroxyapatite composites

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Abstract

The improvement of mechanical properties of HA with reinforcement of 5 and 10 wt.% bioglass (45S5) for different sintering temperatures was studied. Naturally produced HA from human teeth is sintered with the addition of 5 wt.% and 10 wt.% bioglass at 1200 and 1300 °C for 4 h. The microhardness measurements, density and compression tests were performed and microstructural characterizations were carried out by scanning electron microscopy and X-ray diffraction analysis in order to find the optimum sintering temperature. Finally average hardness value of 383±60 HV, average density of 2.72±0.01 g/cm^3, and compressive strength value of σ_{avr}=83.03±33 MPa were achieved by sintering at 1200 °C with the addition of 10 wt.% bioglass in HA. This effect can be attributed to formation of $Ca_5(PO_4)_2SiO_4$ based phases whereas increasing the sintering temperature also resulted in formation of Na_2HPO_4 $7H_2O$ phases which is responsible for decreasing mechanical properties.

Keywords: A. Sintering; Characterization; Bioglass; Hydroxyapatite; Composite materials

1. Introduction

Composites have been a subject of interest during the last four decades. The goal for development of such materials has been to achieve a combination of properties not achievable by any of the elemental materials acting alone. Autograft and allograft are typically utilized as defect fillers, however with the former, increased morbidity, operative time, blood loss, and a finite supply may limit its use. Allograft introduces the potential for disease transmission and immunological response and may fail to fully remodelling leading to mechanical failure. Neither autograft nor allograft provides optimal mechanical support for juxta-articular defects and ceramic bone graft substitutes including β-tricalcium phosphate, HA, or their combinations, have excellent biocompatibility and have been used experimentally and clinically for filling bone defects [1].

Hydroxyapatite (HA) belongs to a group of calcium phosphates, which are being considered as bone substitute materials, which will not cause defensive bodily reactions, and will even establish interactions with the body. The composition of HA is $Ca_5(PO_4)_3OH$ with the ratio that calcium bears to P equivalent to 1.67. The density without porosity of HA is approximately 3.16 g/cm^3, the hardness is approxiamety 500 HV, the compressive strength is between 100 and 200 MPa and its fracture toughness is 1 MPa m$^{1/2}$. Resulting from this that HA cannot be considered as a high strength material compared to the implant materials such as aluminium oxide ceramics or titanium [2]. HA shows good biocompactibility with human body but its applications are limited to non-load-bearing areas due to its low mechanical properties [3].

Bioglasses, are highly bioactive ceramics and their bioactivity has been demonstrated both in vitro and in vivo, with the formation of a strong bonding with the neighboring bone. However, medical applications of bioglass have been centered on low stress fields, mainly due to its non-adequate fracture toughness compared to that of cortical bone. This limitation is unfortunately a common characteristic of glasses, ceramics and glass ceramics used in medical applications [4]. The density of bioglasses is approximately 2.45 g/cm^3; they have a

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hardness of 458 HV, mechanical strength of 100–200 MPa and 1.2–2.6 MPa $m^{1/2}$ fracture toughness. They can carry on their mechanical properties in vitro and in vivo more space of time than HA [5]. Bioactivity of bioglasses is also higher than that of HA. It is assumed that the presence of bioactive glassy phase can provide faster response in terms of bone healing and bonding processes. It is also observed that glass-reinforced HA composites exhibit greater biological activities than commercial HA [6].

In this study, the effects of bioglass addition into HA on mechanical properties are investigated for different sintering temperatures.

2. Materials and methods

The HA material was derived from extracted deproteinized human teeth with calcination at 850 °C for 3 h. Easy separation of the dentine and enamel matter has been observed at that temperature. The 60% of the matter was dentine and 40% is enamel. These parts were subjected to grinding with a blade grinder for 30 s separately. 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 study.

The bioglass compositions were prepared from 45 wt.% SiO_2, 6 wt.% P_2O_5, 24,5 wt.% Na_2O, 24,5 wt.% CaO known as 45S5. The compositions were placed in platinum crucible and heated to 1330 °C for 4 h. Subsequently they were poured into water in order to be in granular form. They were milled to a powder type particle in a porcelain ball milled for 24 h [3].

Bioglass powders with an average particle size of 100–130 μm were mixed by 5 and 10 wt.% with HA. Firstly acetone and HA were wet milled together for 24 h. 5 and 10 wt.% bioglass were correspondingly mixed with HA and ball milled with acetone. A die was designed in order to prepare samples with a diameter of 11 mm according to British Standards. After the compaction, powders were subjected to sintering at 1200 and 1300 °C for 4 h.

The microhardness measurements (200 g load), the density (Archimedes Method), and compression tests (DEVOTRANS DVT 621) were carried out in order to find the optimum sintering temperature. Scanning electron microscopy (JOEL 35 MT 330 SEM) and X-ray diffraction analysis method were used to characterize microstructure and phases.

3. Results and discussion

Typical microstructure of bioglass–HA composites is given in Fig. 1 for a sample containing 10 wt.% bioglass reinforcement and sintered at 1200 °C. It seems that certain amounts of porosity, glassy phase and HA matrix is existing. The X-ray diffraction analysis results of this sample showed that main phase of this sample is basically calcium phosphate silicate (Fig. 2).

Microhardness, density and compression test results depending on reinforcement content for HA–bioglass composites are listed in Table 1. Results indicated that physical and mechanical properties of HA–bioglass composites are between that of HA and bioglass sintered bodies as reported in the introduction part.

Variations of density of composites depending on reinforcement contents and sintering temperatures are shown in Fig. 3. It seems that increasing the bioglass reinforcement content from 5 to 10 wt.% resulted in increasing the density of composite from 2.66 to 2.72 whereas same effect could not be observed when the

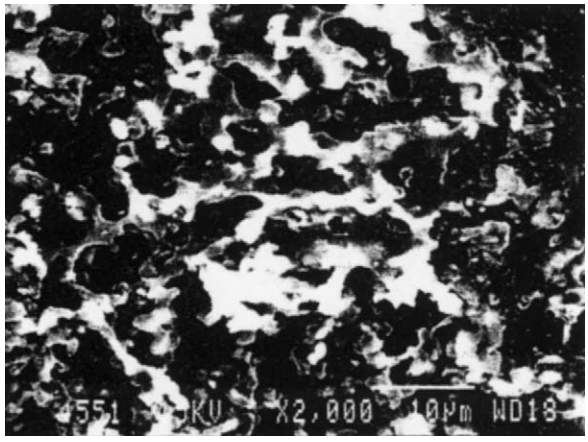

Fig. 1. SEM photograph of 10 wt.% bioglass added HA sintered at 1200 °C.

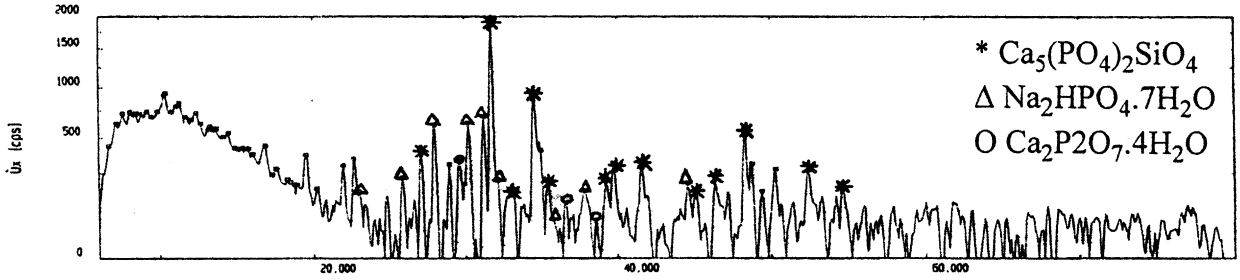

Fig. 2. X-ray diffraction pattern of the HA containing 10 wt.% bioglass sintered at 1200 °C.

Table 1
Sintering results of HA-bioglass composites in two sintering temperatures

Temperature (°C)	Reinforcement content (wt.%)	$Density_{avr}$ (g/cm^3)	$Hardness_{avr}$ (HV, kg/mm^2)	Compressive $strength_{avr}$ (MPa)
1200	5	2.66±0.05	472±66	62.23±20.29
1200	10	2.72±0.02	383±38	83.03±33.95
1300	5	2.72±0.01	365±60	68.81±9.72
1300	10	2.73±0.028	234±32	43.38±5.14

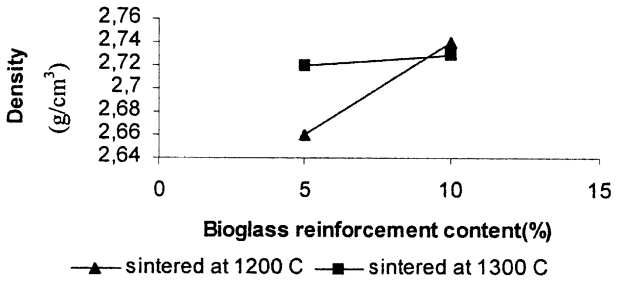

Fig. 3. Variations in density for 5 and 10 wt.% bioglass reinforced HA at different sintering temperatures.

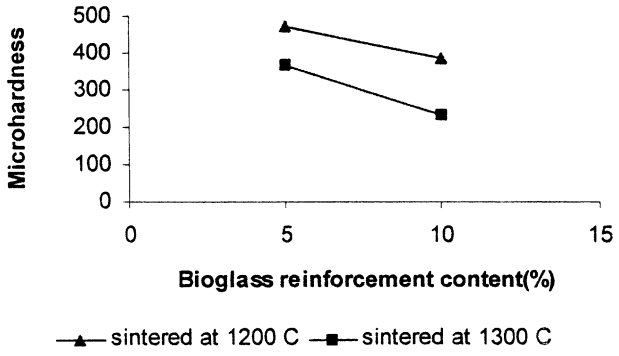

Fig. 4. Variations in microhardness for 5 and 10 wt.% bioglass reinforced HA at different sintering temperatures.

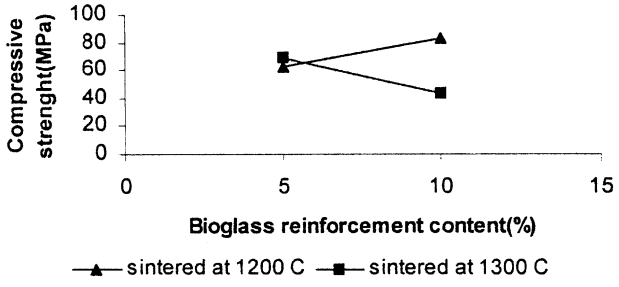

Fig. 5. Variations in compressive strength for 5 and 10 wt.% bioglass reinforced HA at different sintering temperatures.

sintering temperature was increased from 1200 to 1300 °C. It seems that increasing of reinforcement content did not result in the increase of density, which was about the same level as 2.72 for 5 and 10 wt.% bioglass reinforcement for sintering at 1300 °C (Fig. 3).

On the other hand, it is clearly observed that increasing the sintering temperature decreased the microhardness of composites depending on reinforcement content for both sintering temperature (Fig. 4). The figure indicates that increasing the bioglass content of composite from 5 to 10 wt.% causes a decrease of the hardness of composite from 472 and 383 HV for sintering at 1200 °C. Meanwhile the same effects were also observed when the sintering temperature is increased. Increasing the bioglass reinforcement content from 5 to 10 wt.% decreases the hardness of composite from 365 to 234 for sintering at 1300 °C.

Variation of compressive strength depending on reinforcement content for both sintering temperature is given in Fig. 5. The figure shows that increasing reinforcement content from 5 to 10 wt.% increased the compressive strength from 62 to 83 MPa for sintering at 1200 °C, whereas a decrease on compressive strength was observed to exist from 68 to 43 MPa with the addition of 5 to 10 wt.% bioglass for sintering at 1300 °C. Such a phenomenon can be attributed to the occurrence of a new phase between bioglass and HA for higher sintering temperatures.

It is stated in literature that critical sintering temperature for HA is 1300 °C [3]. Above this temperature HA structure will collapse, alpha and beta tricalcium phosphate phases occur. In fact sintering of natural hydroxyapatite resulted in compressive strength value of 56.30 and 56.77 MPa at 1200 and 1300 °C respectively [6]. On the other hand average compressive strength of 68.81 MPa has been reached by adding 5% wt. bioglass whereas increasing of bioglass content from 5 to 10 wt.% were resulted in decreasing of compressive strength to 43.38 MPa at 1300 °C. The results of another research regarding to processing of HA-bioglass composites also stated that sodium content of bioglass is tended to react with TCP phases for sintering at critical temperature [7]. The decrease of mechanical properties with the increasing of sintering temperature for this research can be explained with the formation of sodium and TCP based compounds. Meanwhile X-ray diffraction analysis results of composite are in close agreement with this claim. It seems that increasing of sintering temperature increases the amount of Na_2H-$PO_4.7H_2O$ phase at 1300 °C (Fig. 6). Whereas X-ray diffraction analysis results of composite having best mechanical properties indicates that main phase is

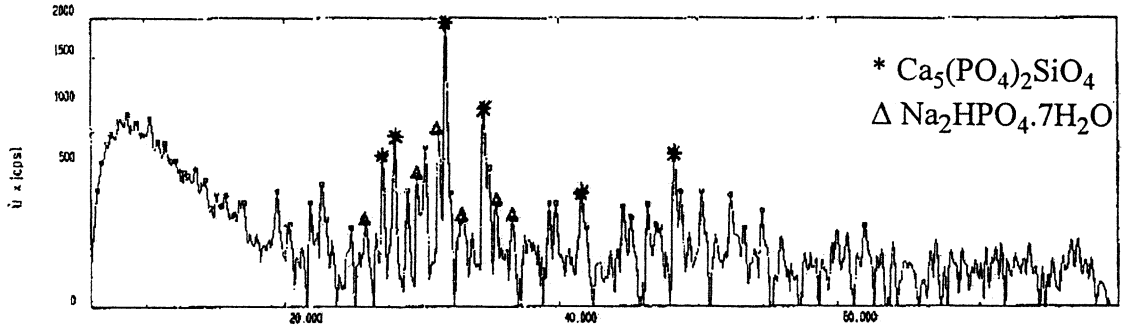

Fig. 6. X-ray diffraction pattern of the HA containing 10 wt.% bioglass sintered at 1300 °C.

calcium phosphate silicate [$Ca_5(PO_4)_2SiO_2$] which is sintered with the addition of 10 wt.% bioglass into HA at 1200 °C (Fig. 2).

4. Conclusion

From this study it can be concluded that the average hardness value of 383 HV, the average density of 2.72 g/cm^3, and the compressive strength value of $\sigma_{avr} = 83.03$ MPa were achieved by sintering at 1200 °C with the addition of 10 wt.% bioglass in HA.

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References

[1] R.D. Welch, B. Hudson, et al., Biomaterials 20 (2002) 464.
[2] G. Willmann, Interceram, High-Performance Ceramics 42 (1993) 206.
[3] F.N. Oktar, G. Göller, Ceram. Int. 28 (2002) 617–621.
[4] M. Amaral, M.A. Lopes, R.F. Silva, J.D. Santos, Biomaterials 23 (2002) 857.
[5] A.O.Keskin, Improving the Mechanical Properties of Hydroxyapatite Ceramics by Zr Reinforcement, MSc Thesis, Istanbul Technical University, Istanbul, 2000.
[6] G. Goller, F.N. Oktar, Mater. Lett. 56 (2002) 142–147.
[7] J.D. Santos, J.C. Knowles, R.L. Reis, F.J. Monteino, G.W. Hastings, Biomaterials 15 (1) (1994) 5.