



Effect of type of calcium phosphate on microstructure and properties of glass reinforced biocomposites

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Abstract

In the present study two different types of calcium phosphates (synthetic calcium phosphates (SCP) and biogenic hydroxyapatite (BHA)) were used to produce porous biocomposites with addition of 35.5–41.0 wt % $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ glass. It has been shown that morphology, density, porosity, mechanical properties and solubility in vitro of prepared composites depend on the amount of glass and type of introduced phosphates. The obtained results reveal that the prepared composites combine good mechanical properties (up to 141 MPa) with sufficient solubility. The porous composites based on SCP have a significant higher dissolution in physiological solution in comparison with composites based on BHA.

Keywords: hydroxyapatite, glass, morphology, porosity, solubility

I. Introduction

Biocomposites have been a subject of great interest of researchers and surgeons during the last years. 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.

Porous hydroxyapatite (HA) implants have been widely used in various fields of medicine (orthopedics, maxillofacial surgery, etc.) and have demonstrated bone in-growth into the open pores on the surface of the implant [1,2]. HA samples sintered at $T < 1000^\circ\text{C}$ have shown good biocompatibility with human body, but its application is limited due to its low mechanical properties [3,4]. One way to improve the HA ceramics is the addition of a $\text{CaO-P}_2\text{O}_5$ based glass as a second phase. Bioglasses are highly bioactive materials and their bioactivity has been demonstrated both *in vitro* and *in vivo* due to the formation of a strong bonding with the neighboring bone [5]. It is observed that glass-reinforced HA composites exhibit better mechanical properties and dissolution than HA ceramics [6–9].

The aim of the present study was fabrication and the comparative investigation of the microstructure and properties of composites based on synthetic calcium phosphates and biogenic hydroxyapatite prepared at

the same conditions with addition of $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ glass.

II. Experimental Procedure

Two different calcium phosphate powders were prepared according to the procedure proposed in earlier work [10]. The BHA (biogenic hydroxyapatite) used in this study was derived from animal bone at $\sim 800^\circ\text{C}$; the SCP (synthetic calcium phosphates) powder was obtained using the chemical precipitation from calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and ammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$.

The glass-reinforced biocomposites based on SCP (SCP-Glass) and BHA (BHA-Glass) are prepared by a liquid phase sintering process with the addition of 35.5–41.0 wt % $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ glass to the SCP and BHA powder [11]. The biocomposite composites are given in Table 1. SCP or BHA powder and glass-forming components were mixed and primary sintered at $T_1 \leq 1100^\circ\text{C}$. The primary sintered composites were milled, sieved and uniaxially pressed at 150 MPa to form disc-shaped samples. The green compacts were sintered at $T_2 \leq 800^\circ\text{C}$.

Density measurements of prepared composites were performed in the toluene using the Archimedes principle. X-ray diffraction, XRD (DRON-1.5, Bourevestnik Inc., Saint-Petersburg, Russia) was used to study the phase compositions and transformations in the compos-

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ites. Powders morphology was examined by transmission electron microscopy, TEM (JEM–2100-F, JEOL Inc., Tokyo, Japan). Composite microstructures were investigated using a scanning electron microscopy, SEM (JSM–5400, JEOL Inc., Tokyo, Japan). Longitudinal lengths of some crystalline blocks were measured using the image analysis software with SEM images loaded to a computer.

To estimate a solubility of composite materials, each sample was immersed in the physiological solution for 2, 5 and 7 days at 36–37°C and their degradation in solution was measured by a sample mass loss. Mechanical compressive strengths of samples were determined depending on their composition and degradation in the physiological solution.

III. Results and Discussion

TEM micrographs (Figs. 1 and 2) show particles of nanometric size of the SCP (105–305 nm) and the BHA powders (85–140 nm). Powder morphology consists of nearly spherical nano-aggregates (205–575 nm in diameter) and agglomerates (0.5–160 µm in diameter) for both types of composites. XRD results of these powders showed that main phase of BHA is HA and phases present in SCP are HA, β -tricalcium phosphate (TCP), tetracalcium phosphate (TeCP) and β -calcium pyrophosphate (CPP). The β -calcium pyrophosphate

(CPP) phase becomes unstable and tends to decompose at sample sintering temperature T_2 . The X-ray diffraction analysis results of the BHA-Glass samples showed that their HA crystal phase did not transform into the TCP structure after sintering in contrast to phosphate glass-reinforced HA composites [6–9].

Typical microstructures of the SCP-Glass and BHA-Glass composites are given in Figs. 3 and 4 for the sample containing 38.3 wt % of $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ glass. It seems that certain amounts of pores, crystalline blocks and amorphous glass exist in composite microstructure. Sometimes it is possible to observe the crystalline blocks of regular geometrical shape. According to the image analysis software applied to SEM images it was determined that the average sizes of crystalline blocks were approximately up to 2.2 µm in a cross-section and up to 12.6 µm in a length for the SCP-Glass and BHA-glass samples (Table 1). The formation of the monoblock structure during secondary sintering in presence of liquid glass phase in both types of the composites can be attributed to the recrystallization process of HA structure.

Results of density and porosity measurements, depending on glass contents, for the SCP-Glass and BHA-Glass composites are listed in Table 2. The results indicate that increasing of the glass content of composite from 35.5 to 41.0 wt % causes an increase of the com-

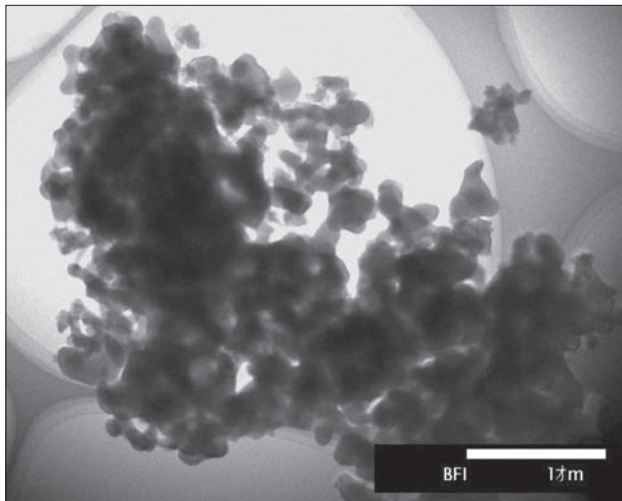


Figure 1. TEM micrograph of SCP powder (bar = 1µm)

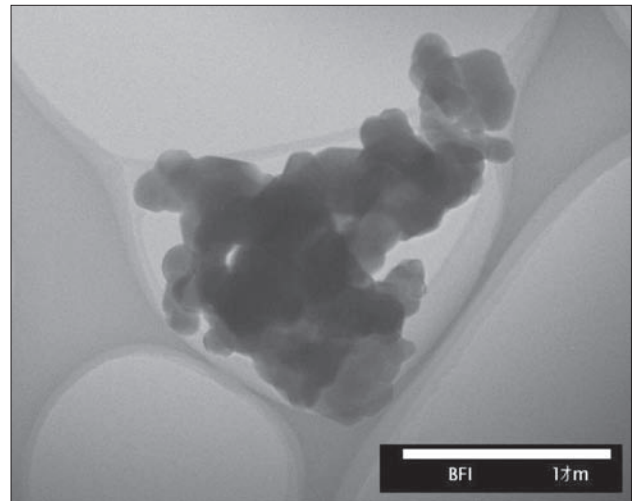


Figure 2. TEM micrograph of BHA powder (bar = 1µm)

Table 1. Composition and some microstructure parameters of SCP-Glass and BHA-Glass biocomposites

Material	Type of calcium phosphate	Portion of glass [wt %]	Mean crystalline block size [µm]	Mean pore size [µm]
SCP-Glass-8	HA, TCP, TeCP	41.0	–	–
SCP-Glass-9	HA, TCP, TeCP	38.3	–	0.93–11
SCP-Glass-10	HA, TCP, TeCP	35.5	2.9–11.4	0.77–20.2
BHA-Glass-8	BHA	41.0	–	–
BHA-Glass-9	BHA	38.3	4.0–11.0	0.7–3.2
BHA-Glass-10	BHA	35.5	2.2–12.6	0.54–14

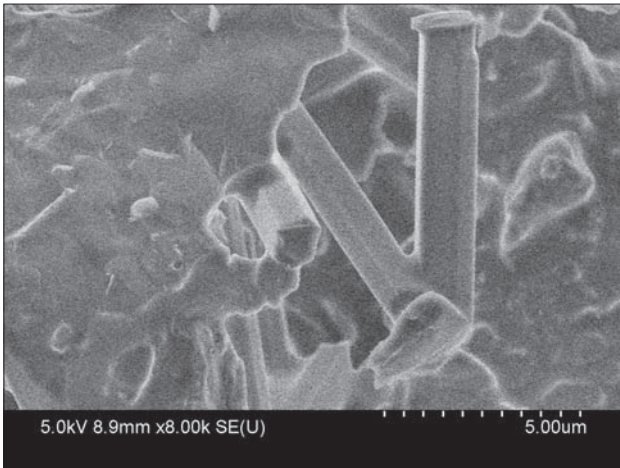


Figure 3. SEM micrograph of SCP-Glass-10 composites (bar = 5µm)

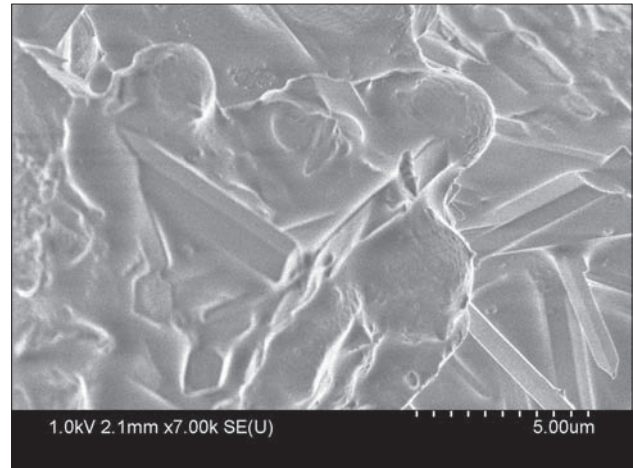


Figure 4. SEM micrograph of BHA-Glass-10 composites (bar = 5µm)

Table 2. Some properties of prepared samples

Material	Pycnometric density (±0.007) [g/cm ³]	Porosity (±0.25) [%]	Compressive strength (±8) [MPa]	Solubility after 7 days [% mass loss]	Compressive strength after soaking for 7 days (±8) [MPa]
SCP-Glass-8	2.86	28.3	135	10.079	37
SCP-Glass-9	2.90	29.4	131	6.426	44
SCP-Glass-10	2.92	30.0	108	7.563	48
BHA-Glass-8	2.70	25.1	141	1.510	151
BHA-Glass-9	2.76	26.0	128	1.926	128
BHA-Glass-10	2.78	27.2	98	2.009	117

posite density up to 2.92 g/cm³ and 2.78 g/cm³ for SCP-Glass and BHA-Glass composite, respectively (Table 2). Meanwhile, the same tendencies were also observed for mechanical compressive strength. Increasing the glass content increases the mechanical compressive strength and decreases the porosity for both types of composites (Table 2). It seems that the porosity and compressive strength of the SCP-Glass and the BHA-Glass samples with the same amount of the glass phase are nearby.

Figs. 5 and 6 present the solubility *in vitro* for the SCP-Glass and BHA-Glass composites, respectively.

Results indicate that the SCP-Glass composites have significantly higher solubility *in vitro* (3–24 times) compared to the BHA-Glass composites. Such a phenomenon can be attributed to the considerable higher solubility of their crystalline content, in particular TeCP phase. There is significant dependence of solubility on the amount of BHA for the BHA-Glass composites (Fig. 5). In addition, solubility of the BHA-Glass composites increases with immersion time (Fig. 5). However, for the SCP-Glass composites there is more complex dependence of the solubility on the SCP content (Fig.

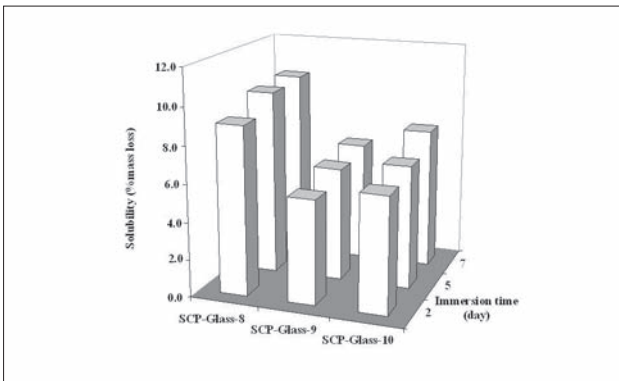


Figure 5. Variation in solubility (% mass loss) for SCP-Glass composite after immersion in physiological solution

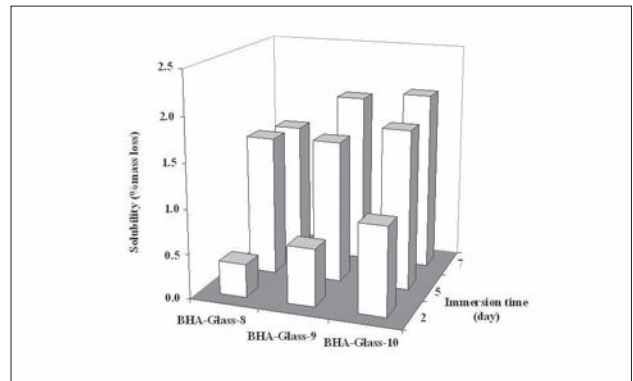


Figure 6. Variation in solubility (% mass loss) for BHA-Glass composite after immersion in physiological solution

6) and their solubility practically does not change with time. That phenomenon can be attributed to various natures of surface physical-chemical interactions between crystalline particles and glass phase in both types of composites. The investigations of this interaction are still in progress.

These results evidence that combination of mechanical properties and solubility of the SCP-Glass and BHA-Glass composites are in good agreement with analogous properties of the known HA and the glass reinforced HA materials [2,4]. The investigated biocomposites have an optimum combination of the compressive strength and the solubility, and may be use in medicine as biomaterials for replacing bone cavities.

IV. Conclusions

The porous SCP-Glass and BHA-Glass composites have been prepared by sintering the phosphate powders with 35.5–41.0 wt % of the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ glass and comparatively investigated. It can be concluded that the character of microstructure and porosity, pycnometric density and compressive strength values for both types of composites were similar, but the SCP-Glass samples showed significant higher solubility *in vitro* in comparison to the BHA-Glass ones and more complex dependence on the composition. The prepared materials combine the good mechanical properties with the sufficient solubility and may be potential candidates as bioactive implant materials for filling bone cavities.

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