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Effect of Al_2O_3 addition on bioactivity, thermal and mechanical properties of some bioactive glasses

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Abstract

Three bio-phosphate glass-specimens with and without Al_2O_3 addition were prepared in order to shed light on their bioactivity behavior towards the simulated body fluid biological solution (SBF). The results revealed that Al_2O_3 has significant effect on the ability of bio-glass to form the hydroxycarbonate apatite layer on its surface. That layer was detected by FTIR spectra, SEM micrographs and EDAX pattern. Also, the effect of Al_2O_3 on the mechanical properties was studied by measuring the hardness of the glass samples, which increased by Al_2O_3 addition. The thermal expansion coefficient was decreased by increasing the Al_2O_3 percent in the bio-glass samples.

Keywords: D. Al_2O_3; D. Glass; E. Biomedical applications; Physical properties

1. Introduction

Bioactive ceramic was discovered recently, and since then has given rise to new strategies as artificial materials in clinical bone repairs and replacement. The bioactive ceramics spontaneously bond to and integrate with living bone in the body without fibrous tissue forming around them. Hench et al. [1,2] were the first authors who introduced the idea of firmly bonding bone with synthetic materials through the chemical reactions that take place on a glass surface when it is implanted into a living body.

The characteristic amorphous quality of glass is its open structure arrangement which facilitates the inclusion of cations referred as network modifiers, causing a discontinuity of the glassy network and consequently, non-bridging oxygen is released. This disordered structure, enhanced by the presence of network modifier, gives rise to the high reactivity of glass in aqueous environments. This high reactivity is the main advantage of their application in periodontal repair and bone augmentation. This is due to the reaction [3] products obtained from these types of glasses and physiological fluids resulting in crystallized apatite-like phase similar to the inorganic component of bones in vertebrate species [4].

Bioactive glasses, from their beginnings in the 1970s, have reached a significant level of development, resulting since their discovery in the preparation of different compositions of such kind of glass.

Silicon-free bioactive glasses have the advantage of being close [5] to the composition of natural bone, but their disadvantage lies in their low mechanical strength which limits their applications. Invert phosphate glasses based on the system $Na_2O/CaO/P_2O_5$ have been developed as resorbable biomaterials which can be considered as regenerator of bony defects, and favored [6] compared with bone substitutes. These resorbable materials can be dissolved after necessary time to fill the defect with new bone, without any toxic effect on the human life. Hydrolytical durability is often an important property required for the glass. However, glasses which are intended to be used in the human body as implant materials and become attached to living tissue must have certain solubility. Also, for long-term implants, it may be important to decrease the solubility as much as possible without losing bioactivity. This in turn requires an understanding of how compositional changes influence the solubility and bioactivity [7]. On the other hand, bio-absorbable materials which degrade and absorb in the human body (phosphate glasses) are useful as suture thread in bone fracture fixation applications and as carriers in drug delivery.

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Table 1
Phosphate glass composition

Glass no.	P_2O_5	CaO	Na_2O	Al_2O_3
P8	65	20	15	0
P30	64.5	20	15	0.5
P31	63	20	15	2

Generally, the addition of Al_2O_3 improves the long-time stability of the implants needed for bone defect repairing. In this work, phosphate glasses were prepared with different Al_2O_3 additions to study their effect on the bioactivity, chemical, thermal and mechanical properties of the parent glass.

2. Experimental procedures

2.1. Preparation of bioactive glasses

Three bioactive glass samples were prepared from $Ca(H_2PO_4)_2$, $CaCO_3$, Na_2CO_3 and Al_2O_3 reagent grades according to the compositions shown in Table 1. The raw materials were mixed and melted in porcelain crucible at 1000–1150 °C for 1 h. All glasses were casted as blocks in heated stainless-steel molds, annealed at 350 °C and cooled to room temperature. Those samples designed as P8, P30 and P31.

2.2. Bioactivity studies

To study the bioactivity, each glass sample was soaked in 50 ml of tris-buffered simulated body fluid (SBF) solution, which resembles the human blood plasma, at 37 ± 0.5 °C, for 2, 7 and 14 days. The ions concentration of SBF and body plasma is summarized in Table 2. The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 into deionized water. The solution was buffered to pH 7.4 with tris-(hydroxyl methyl)-amino methane [$(CH_2OH)_3CNH_3$] and hydrochloric acid. The immersed glass samples were taken out after immersion in (SBF), washed with deionized water and finally air-dried. Their surface analyses were conducted by Fourier transmission IR (FTIR) using FTIR spectrometer (type Jasco FT/IR-430, Japan) and scanning electron microscope (SEM mode Philips XL30) attached with EDAX unit.

Changes in the concentration of calcium and phosphorous of the SBF solution due to soaking of the samples for 2, 7 and 14 days were measured using inductive coupled plasma (ICP, Atomic Absorption Spectrometer, Spectra AA).

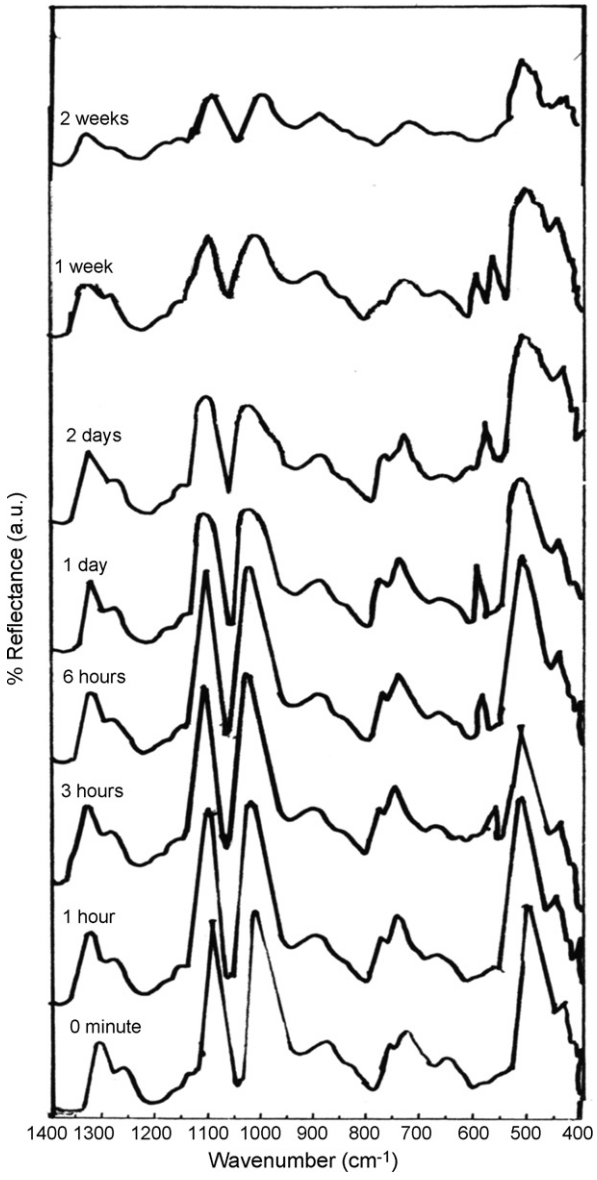

Fig. 1. The FTIR spectra of blank glass (P8) before and after immersion in SBF, from 1 h to 14 days.

2.3. Properties of the bioactive glass

Thermal expansion coefficient of the investigated glasses was carried out on 1.5–1.9 cm long rods using Linseis L76/1250 automatic recording multiplier Dilatometer with heating rate of 5 °C/min. The linear thermal expansion coefficient was automatically calculated using the equation:

$$\alpha = \frac{\Delta L}{L} \times \frac{1}{\Delta T}$$

Table 2
Ion concentration (mM) in the simulated body fluid and human plasma

Ion concentration (mM)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Simulated fluid	142	5	1.5	2.5	147.8	4.2	1	0.5
Body plasma	142	5	1.5	2.5	103	27	1	0.5

where ΔL is the increase in length, ΔT the temperature interval over which the sample was heated and L is the original length of the specimen.

The microhardness of the investigated samples was measured using Vicker's microhardness indentor (Shimadzu, Type-M, Japan). The eyepiece on the microscope of the apparatus allowed measurements with an estimated accuracy of ± 0.5 μm for the indentation diagonals. Grinding and well polishing were necessary to obtain polished, smooth and flat parallel surfaces glass samples before indentation testing. At least five indentation readings were made and measured for each sample. Testing was conducted with a load of 100 g and loading time 15 s. The measurements were carried out under normal atmospheric conditions. The Vicker's microhardness value was calculated from the following equation:

$$H_v = A\left(\frac{P}{d^2}\right) \text{kg/mm}^2$$

where A is constant equal to 1854.5, taking into account the geometry of squared based diamond indentor with an angle 136° between the opposing faces, P the applied load in gram and d is the average diagonal length (μm).

The densities (ρ) of glasses were determined by the Archimedes method and calculated according to the following equation:

$$\rho = \left(\frac{a}{a-b}\right) \times 0.86$$

where ρ is the density, a the weight of sample in air and b is the weight of sample in xylene which its density is 0.86.

The average total rates of glass dissolution (chemical durability) were carried out using bulk glasses. Rectangular slabs of glass with the dimensions 4 cm × 1.25 cm × 0.5 cm were finally polished and used in this test. Before testing, the surface area and weight of the glass samples were measured. The samples were then immersed in 250 ml polyethylene beaker containing different selected solutions (0.05N HCl or NaOH) at 37 °C for 7 days. After immersion, the glass samples were removed; rinsed with distilled water, dried at 110 °C for 2 h and finally reweighed after corrosion. The weight loss has been determined by subtracting the weight of the treated sample from their original weight. Dissolution rates were calculated from the surface area, dissolution time and weight loss using the following equation:

$$\text{rate of dissolution} = \frac{\text{weight loss (g)}}{\text{surface area (cm}^2) \times \text{time (h)}}$$

3. Results and discussion

It is well known that the phosphate glasses have unique properties and crystallization behavior [8]. These facts make them candidates for a variety of special applications such as biomedical materials. However, so far, to our knowledge, the formation of apatite on phosphate glasses without silica has not

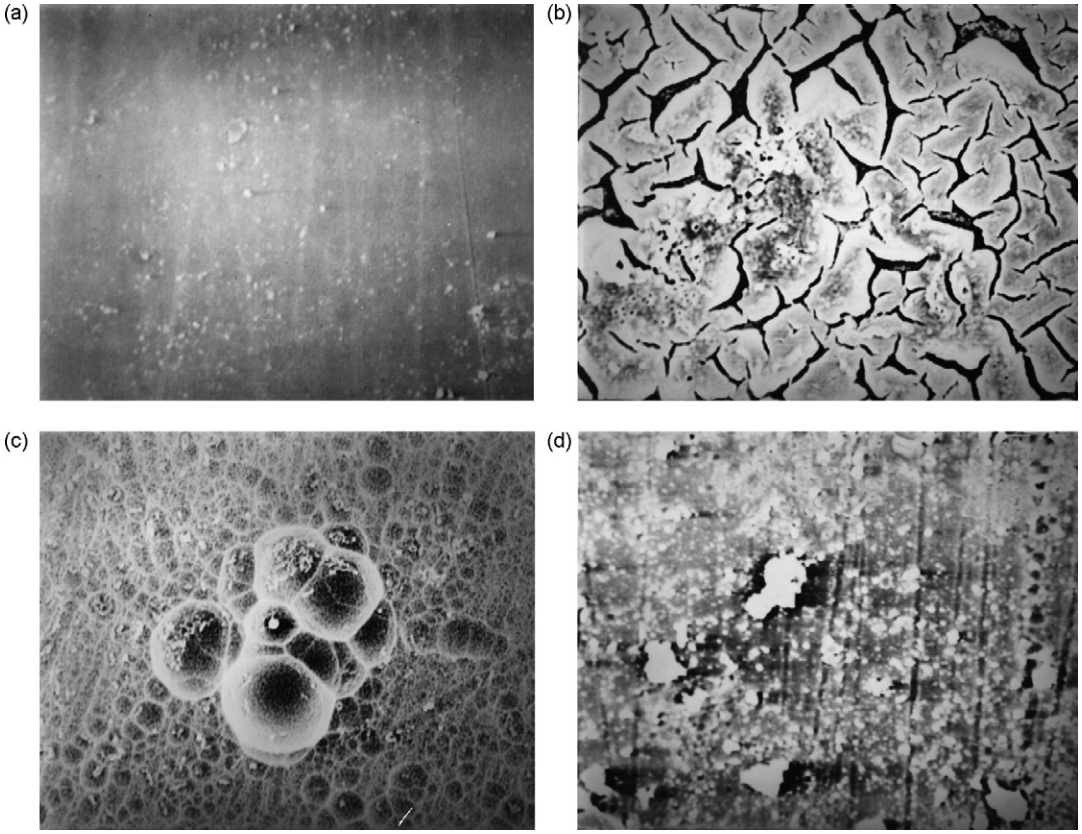

Fig. 2. SEM of the blank glass before and after immersion in SBF for: (a) before immersion, (b) after 2 days immersion, (c) after 7 days immersion and (d) after 14 days immersion.

been detailed reported. For example, it has been reported that, a calcium phosphate invert glass that contained TiO_2 formed a new calcium phosphate apatite layer on its surface after 20 soaking days in simulated body fluid [9].

Fig. 1 shows the FTIR spectra of P8 before and after soaking in SBF solution. From this figure it can be seen that, by increasing the soaking time of the glass sample in SBF, the hydroxycarbonate apatite (HCA) layer begins to crystallize and appears at 560 and 602 cm^{-1}. These peaks start to appear after 3 h soaking and disappear after prolonged soaking time (14 days), which indicated that, the dissolution of glass involves reactions, most notably leaching and network dissolution. When phosphate bioactive glasses immersed in body fluid, sodium, calcium and phosphorous are rapidly leached [7]. Due to this soluble nature of the phosphate glass, the hydroxycarbonate apatite layer is short lived and subsequently disappears after long-time immersion in SBF. Bioactivity can be controlled by optimizing and design the glass composition, even using phosphate glasses [10].

The characterizing peaks of FTIR spectrum (Fig. 1) could be summarized as follows:

(a) Peaks at 1320 and 1275 cm^{-1} are assigned as PO_2 asymmetric stretching vibration modes, while the peaks at 1103 and 1022 cm^{-1} are assigned as PO_3 asymmetric and symmetric stretching vibration, respectively.
(b) The double peaks at 774 and 742 cm^{-1} are due to symmetric stretching vibration of P–O–P group, while that at 893 cm^{-1} to asymmetric one.
(c) The peaks at 666 and 515 cm^{-1} are assigned as the bonding vibration of P–O bonds.

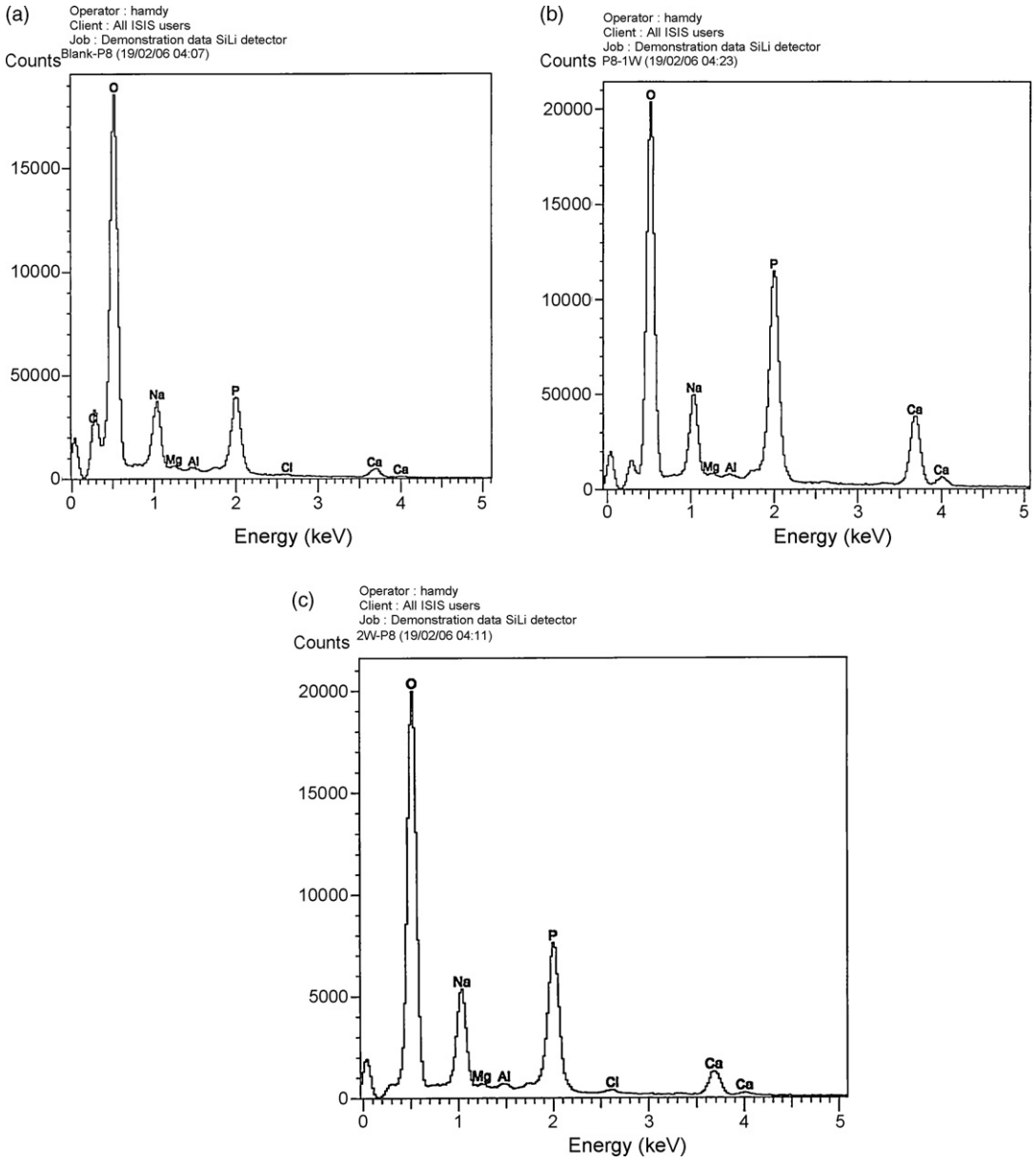

Fig. 3. EDAX pattern for the blank glass surfaces before immersion (a) and after immersion in SBF for 7 days (b) and 14 days (c).

After 7 days immersion in SBF solution, the intensities of the characteristic peaks of metaphosphate units decrease. This is due to the formation of hydroxycarbonate apatite layer (at 602 and 560 cm^{-1}) on the glass surface which disappeared after 14 days soaking indicating its solubility. A new peak was appeared at earlier stages of immersion in SBF solution at 562 cm^{-1}, which is due to carbonate compounds. The presence of this carbonate layer has been shown to be important [11] as it is the precursor layer on which the apatite film appeared. This carbonate compound appeared due to the dissolving nature of the studied glass. This may be the only explanation for the formation of hydroxycarbonate apatite layer, since the formation of bone-like apatite seems to be induced by functional groups existing on materials surfaces, such as Si–OH, Ti–OH, Zr–OH, Nb–OH and Ta–OH [12]. These groups are absent in our glass samples.

Fig. 2 shows the SEM photomicrographs of P8 sample surface before and after immersion in SBF for 2, 7 and 14 days, which confirms the results obtained from FTIR spectroscopy. It appears from the figure that, after immersion in SBF for 2 days (Fig. 2b), traces of amorphous HCA layer are formed. After 7 days immersion (Fig. 2c), granules structure-layer of HCA is observed on the surface. This layer is responsible for the combination between the bioactive material and the bone tissue for optimum healing [13]. After 2 weeks soaking time (Fig. 2d), the layer disappeared completely, which indicates that phosphate bio-glass can be considered as resorbable glass. It is worthy to mention here that the decreasing of P_2O_5 content in glass composition or converting glass to glass-ceramics make it more resistant to dissolve in different solutions; but calcium phosphate-based glasses are designed to degrade gradually over time and can be replaced by the natural host tissue. The prime objective for such materials in vivo is to combine stimulation of osteogenic activity in bone tissues with the capability to be progressively resorbed by specialized bone cells [10].

Fig. 3 shows the EDAX pattern of P8 surface before and after immersion in SBF for 7 and 14 days. The presence of Na, P and minor amount of Ca after immersion in SBF for 7days is recorded. It is clear that the peaks related to P and Ca have been obviously increased due to the precipitation of calcium phosphate apatite layer after 7 days. These peaks sharply decreased after 14 days indicating the gradually disappearing of the apatite layer and confirm both the FTIR spectroscopy and SEM micrographs. As mentioned before, bioactivity can be controlled by optimizing the design of glass composition, even by using phosphate glasses. The addition of Al_2O_3 decreases the solubility of that phosphate glass to acceptable limit which allows the HCA layer to live for longer time on its surface.

It is well known that alumina is generally considered as stabilizer for the glass structure by eliminating some of the non-bridging oxygen [7]. Fig. 4 shows the FTIR spectra of the glass-specimens with and without Al_2O_3 addition (P8, P30 and P31), after soaking in SBF for 2 weeks. From this figure we can deduce the effect of replacing minor amount of P_2O_5 by Al_2O_3 on the formation of the HCA layer on the surface of the bioactive glass. By continuous replacing of P_2O_5 by Al_2O_3, the life time of the HCA layer increases, and the solubility of the glass samples in SBF solution decreases as shown in Fig. 5.

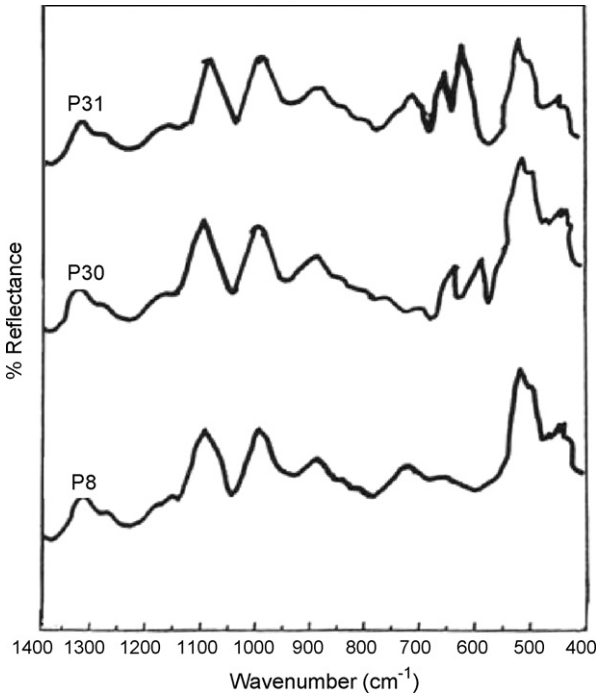

Fig. 4. The FTIR spectra of the glass samples (P8, P30 and P31) after soaking in SBF for 2 weeks.

Fig. 6 confirms the above results. It shows photomicrographs of the glass surfaces (P8, P30 and P31) after 2 weeks soaking in SBF, from which we can see complete disappearing of HCA layer from P8 glass surface (Fig. 6a). Traces of HCA layer still appears on the surface of the P30 (Fig. 6b), while a dense layer of HCA is formed on the surface of P31 (Fig. 6c).

Table 3 summarizes the obtained elemental concentration analysis data of phosphate bio-glass after immersion in the simulated body fluid for different times, i.e. the phosphorous and calcium ions concentration estimated after the immersion. It is obvious that after 2 days immersion, the phosphorous and

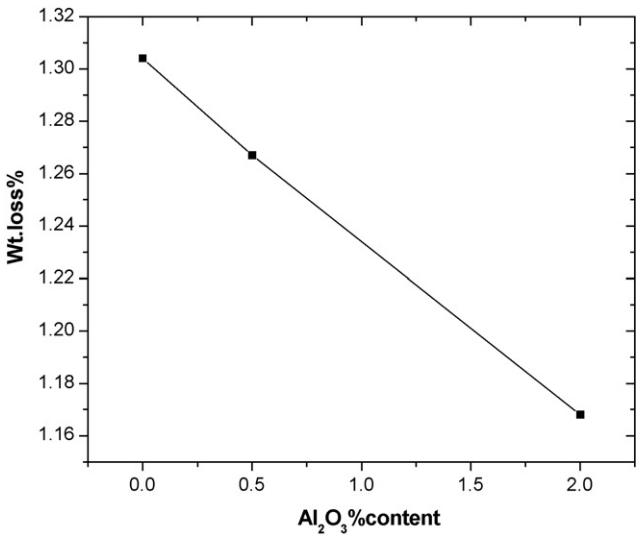

Fig. 5. The solubility of the glass samples in SBF solution for 14 days.

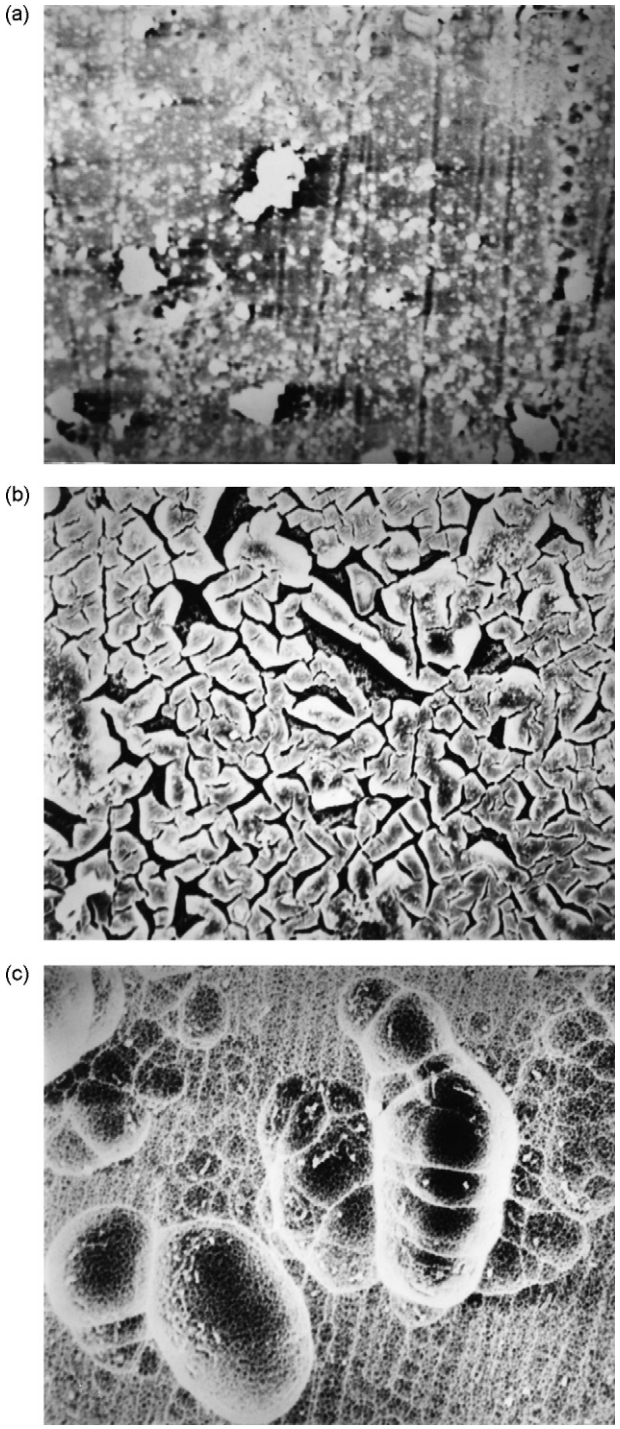

Fig. 6. SEM of the glass samples: (a) P8, (b) P30 and (c) P31 after immersion in SBF for 14 days.

calcium ions concentrations are relatively increased for all studied samples. With prolonging the immersion times to 7 days, the estimated quantity is decreased, while after 14 days it began to increase again. P31 exhibits the lowest phosphorous and calcium ions concentrations. These results can be discussed on the basis of easily dissolving of phosphate glass in aqueous solutions and the fast release of the acidic phosphorous ions at the early times of immersion leads to lowering in the pH value. Generally, calcium phosphate apatite crystals are precipitated

Table 3
Elemental concentrations in the SBF solution after the immersion of glass samples for (2, 7 and 14) days

Sample no.	Time (days)	Elemental concentrations (ppm)	
		Ca	P
SBF (standard)		89.05	34
P8	2	93.9 ± 0.5	38.4 ± 0.5
	7	85.5 ± 0.5	28.7 ± 0.5
	14	90.3 ± 0.5	29.5 ± 0.5
P30	2	92.0 ± 0.5	35.1 ± 0.5
	7	82.9 ± 0.5	25.0 ± 0.5
	14	89.5 ± 0.5	27.0 ± 0.5
P31	2	90.0 ± 0.5	33.1 ± 0.5
	7	80.5 ± 0.5	20.2 ± 0.5
	14	87.9 ± 0.5	25.0 ± 0.5

in alkaline medium [9]. Sample P8 exhibited the higher release of phosphorous ions which decrease the pH of the solution and consequently low the possibility of HCA layer formation especially at long-time of immersion. The presence of Al_2O_3 in P30 and P31, which is responsible for the increase of glass strength towards dissolving in aqueous solutions, led to decrease of phosphorous (P) ions in the solution. The decrease in P ion concentration is due to its consumption in apatite layer formation and to the decrease of glass solubility. The increase of calcium and phosphorous ions in SBF solution at short times is due to their release from the bio-glass. With increasing the time of immersion (7 days), their amounts decrease due to their consumption in the formation of apatite layer. After 14 days immersion, their amounts are little bit increase again due to the dissolution of the formed layer.

Table 4 summarizes the data of measured density, microhardness and thermal expansion coefficient for P8, P30 and P31 glass samples. It appears that the density increase as we go from P8 to P31. This is due to the decrease in non-bridging oxygen [7] after Al_2O_3 addition to the glass samples, which leads to more network compactness. Also the decrease in thermal expansion coefficient (α) can be explained by the change in aluminum coordination in the bio-glass samples, i.e. due to the location [14] of Al^{3+} ions between the phosphate chains and creating a much stronger ionic cross linking and slight increase in the number of octahedrally coordinated Al^{3+} ions which consequently affect the thermal expansion.

On the same grounds, it can be assumed that increasing the bond strength of the ionic link in Al_2O_3 doped bio-glass is

Table 4
Density, microhardness and thermal expansion coefficient (α) of P8, P30 and P31 glass samples

Glass no.	Density (g/cm^3)	H_v	Thermal expansion coefficient, $\alpha \times 10^{7-}$ at 300 °C
P8	2.6454	315	161 ± 2
P30	2.6548	350	157 ± 2
P31	2.6736	373	150 ± 2

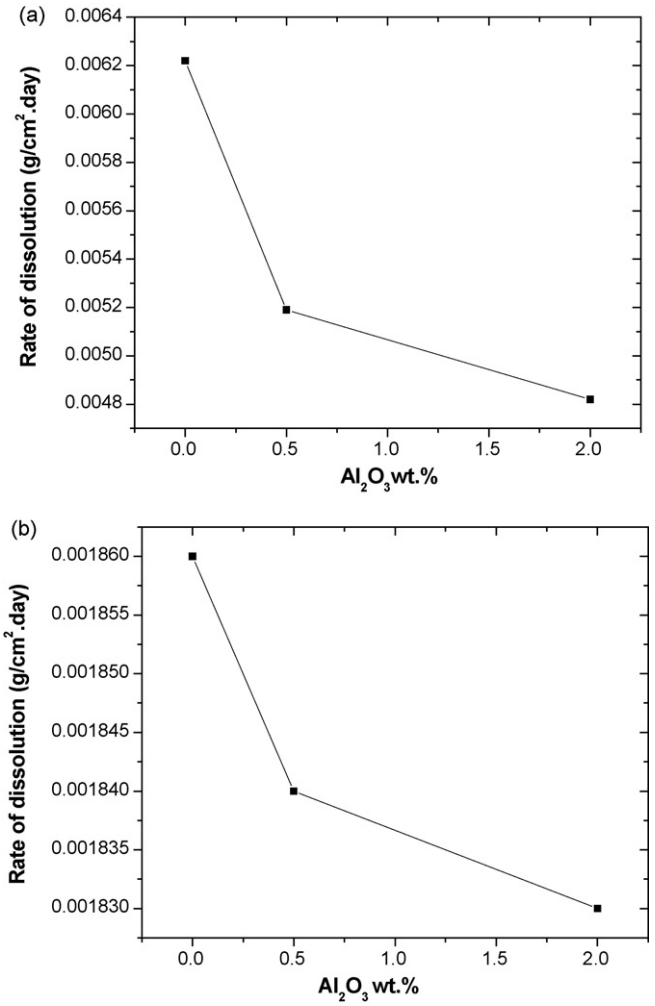

Fig. 7. (a) Rate of dissolution of glass with a different aluminum oxide content after immersion in 0.05N HCl for 7 day vs. Al_2O_3 content and (b) rate of dissolution of glass with different aluminum oxide content after immersion in 0.05N NaOH for 7 days vs. Al_2O_3 content.

expected to strengthen the glass structure and consequently increases the Vicker's hardness [15].

The chemical durability of the bio-glass-specimens was studied by immersing the glass samples in HCl or NaOH (0.05N) for 7 days. Fig. 7(a) and (b) shows the weight loss of the three glass samples versus Al_2O_3 percent added to the parent glass. It can be seen that the weight loss of the glass samples shows little decrease by increasing the Al_2O_3 content indicating that leaching effect of glass decreased and its strength increased [14]. This result is in agreement with the bioactivity behavior of the studied glass samples.

4. Conclusion

The effect of slight addition of Al_2O_3 on the bioactivity behavior of phosphate glass has been studied. The results showed that by gradually addition of Al_2O_3, the bioactivity increased which could be indicated by the acceleration in the formation of hydroxyl carbonate apatite layer on the surface of immersed glass in simulated body fluid. This is attributed to the increase in glass strength and consequently improvement of mechanical, thermal and chemical properties to the studied bio-glass.

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