Bioactivity of CaSiO3 and Porecalin-CaSiO3 Composites
Prepared by Sol-Gel Method for Dental Applications

Asawer Mohsen Hamza¹, Eman Jabber Abed Alshaibani²,* and Rajaa R. Abbas³

¹Dept. of Materials Engineering, Faculty of Engineering, University of Kufa, Najaf, Iraq. E-mail: asawerm.jabeer@uokufa.edu.iq
²Dept. of Materials Engineering, Faculty of Engineering, University of Kufa, Najaf, Iraq. E-mail: iman.alshaibani@uokufa.edu.iq
³Faculty of Dentistry, University of Kufa, Najaf, Iraq. E-mail: rajaa_74@yahoo.com
* Corresponding author: Faculty of Engineering, University of Kufa, Iraq.
Tel: +9647810088057.

Abstract. In this study, the bioactivity of CaSiO3 and Porecalin-CaSiO3 composites have been investigated utilizing X-ray diffraction (XRD) and scanning electron microscopy-Energy-dispersive X-ray spectroscopy (SEM-EDS). CaSiO₃ and P-CaSiO₃ are prepared by Sol-Gel method for different weight percentages of CaSiO₃ (P90CS10, P80CS20 and P70CS30 wt. %). The in vitro bioactive properties have been carried out by immersed the powder and sintered samples on different compositions in simulated body fluids at 32 day to evaluate their bioactivity. Ca/P ratio have been calculated through EDS measurements. Structural characterization revealed the amorphous phase of CaSiO₃ when heated at 700 °C and phase transition to the crystalline phase when heated at 950 °C, where pseudowollastonite (α-CaSiO₃) and Ca₂(SiO₄) phases have been appeared. CaSiO₃ showed better bioactive ability in comparison with its composites. In general, the bioactivity increases with increasing the CaSiO₃ time of immersion in stimulated body fluid (SBF). The closest value to the stoichiometric hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂ has been observed with P70CS30 sintered specimen where Ca/P was 1.694.

Keywords: bioactive ceramics, Calcium Silicate, Porcelain, Sol-gel, Hydroxyapatite, SBF.

1. Introduction.

Bioactive ceramics may be categorized into bioactive glass and bioactive glass-ceramic [1]. Bioactive glasses are silicate-based ceramics with amorphous structure. The first system of bioactive glass was studied by Hench in 1969, it included SiO₂, Na₂O, CaO and P₂O₅ [2] and followed by a series of
bioactive glasses with different ratios and additional elements such as CaO-B2O3 - P2O5 [3] and Na2O-K2O-MgO-CaO-B2O3-P2O5-SiO2 [4].

Binary system of silicate bioceramic (calcium silicate, CaSiO3) was published as a potential biomaterial in 1990 [5]. Calcium silicate can be obtained by reaction of calcium oxide (CaO) with silicon dioxide (SiO2) [6]:

\[ \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \]

In situation of bioactive bioceramics, characterized by their ability to bond directly with the hard tissue by forming a hydroxyapatite layer at the interface between the bioactive ceramic and tissue [7]. Hydroxyapatite material is similar in composition with the minerals phase which involved in bone or tooth structure [8].

In dentistry, when a tooth is missing due to decay, damage, dental carries or trauma, restorative materials have been used to replace the damaged part by an artificial new one [9]. The material which is used as a restorative material should be biocompatible and have no side effects. For many years, porcelain is one of the most restorative materials which has been used for treatment [10]. Dental ceramic (porcelain) known by its low ability to form the apatite layer when it is in contact with living tissue. This is due to its high chemical stability that made it classified as a bioinert ceramic. In fact, the disability of a porcelain to react with the tissue considered as one of the requirement of dental biomaterials that will be in contact with oral tissues to resist degradation in environment with changeable acidic level and temperature. However, using of porcelain as crown, veneer and prosthetic restorative material may have some disadvantages such as the marginal gap that may occur between tooth and biomaterial, failure of restoration and secondary carries [11,12].

In recent years, many studies have been carried out to improve the bioactivity of porcelain by adding a definite amount of bioactive ceramic such as calcium silicate ceramics. It have been found that composites of porcelain-bioactive ceramic have enhanced bioactive and mechanical properties [13,14].

Bioactive dental glass-ceramics (BDGCs) are characterized by the ability to form a good bonding at the material-tissue interface [15]. In general, to use a ceramic in dental applications, it should be biocompatible, durable, good wear resistant, aesthete and easy to customize. Also, it must have the ability to simulate the natural tooth in translucency and strength [16]. Practically, the biological response of tissues to the bioactive materials and in vivo process of hydroxyapatite layer formation can be studied in vitro by immersing the biomaterial in a simulated body fluid (SBF) which has ion concentrations similar to that of blood or cellular fluids [17,18].

The bioactive behavior of bioactive ceramics comes from the components that existence on the surface [19]. With regarding to calcium silicate ceramics, CaO and SiO2 play a rule in apatite formation process [20].

The bioactivity of CS and formation HA results from the reaction between the released bioceramic’s ions Ca2- and Si4+ (in the form of H4SiO4) by the partial dissolution of glass network and that presents in the cellular fluid (or SBF), phosphor ions PO4 3- and OH-. As a result, silica gel will be formed on the surface to be the basic structure for HA formation [21, 22].

Bioceramics can be synthesized by two process; the traditional ceramic process (melt-cast method) and the chemical based process (sol-gel method). In the traditional method, the glass oxides are mixed and melted together at high temperatures up to about 1300°C [23, 24]. Simply, sol-gel rout can be defined as a chemical process to fabricate metal oxide, such as oxides of silicon (Si) and titanium (Ti). It involves formation of a solution (sol: liquid phase), gelation of the sol (gel: diphas, liquid and solid) and removing the solvent by heat treatment. The sol-gel method goes through three steps: hydrolysis, polymerization and drying process. Chemically, for preparing silicate oxides using silicon alkoxide Si(OR)4, sol-gel processing based on the transformation of Si-OR and Si-OH to siloxane compounds by condensation processes [25, 26]. Glasses and ceramics that prepared by sol-gel method appear more enhanced biocompatibility and bioactivity with higher purity and homogeneity than that fabricated by melting method [27]. The high bioactivity comes from the large surface area and the presence of hydroxyl (-OH) groups which stimulate the hydroapatite layer to nucleate when it is in contact with body fluids [27,28]. However, the study of bioactivity of
melt-derived Si ceramic systems displayed that the biological response is limited by the composition, where SiO$_2$ must be lower than 60 mol% [29]. On the other side, many sol-gel Si ceramic systems such as tri-system (SiO$_2$-CaO-P$_2$O$_5$), di-system (SiO$_2$-CaO) and even pure silica show high bioactivity[30], and quick development of hydroxyapatite layer. This research is centered on the decrease the marginal gap that may occur between tooth and biomaterial, failure of restoration and secondary carries by improvement the bioactivity of CaSiO$_3$ and Porecalin-CaSiO$_3$ composites prepared by sol-gel method.

2. Experimental part

The procedures of the experimental part as shown in following steps:

2.1. Material preparation

2.1.1. The CaSiO$_3$ bioactive ceramic preparation

The procedures of the preparation process of 80% SiO$_2$-20% CaO by sol gel method can be described by the following steps:

1. The sol was prepared by using a magnetic stirrer, to mix 25 ml Tetraethyl orthosilicate (TEOS) (Si(OC$_2$H$_5$)$_4$)(China,99.0% purity) in solution of 3.05 ml nitric acid (Mumbai, India, 71% purity)(2M) and 15.8ml H$_2$O. Then after 1hr, amount of 6.48g of Ca(NO$_3$)$_2$.4H$_2$O (Mumbai, India, 99.0% purity) was added to the mixture with continuous mixing for 4hr.

2. The sol was left in a closed container for three days at room temperature to form a transparent gel mass.

3. The resultant gel was transferred to a furnace at 70ºC aging for three days. In this step, the size of the gel is decreased and completely transformed to a solid phase.

4. The solid samples, were placed in the oven for drying for two days at 150 ºC until the color of the sample become white which then grinded using pestle and mortar to form a powder.

5. To nitrate elimination and stabilization, the powder heat treated at 700 ºC for 3hr in electrical resistance furnace with heating rate 13 ºC/min and then left in the furnace to cool to room temperature (5°C/min). In this step the weight of the produced powder was 8.25g.

6. The final step of the preparation process, the resultant materials were grinded using pestle and mortar and then milled by planetary ball mill (SMF-Disk-Top Planetary Ball Miller) for 30 min with milling speed 2700rpm to obtain a ceramic powder with particle size > 63μm.

2.1.2 The porcelain-CaSiO$_3$ composites preparation

Porcelain-CaSiO$_3$ composites samples have been prepared with different weight ratios in the same preparation steps of CaSiO$_3$ ceramic. Porcelain (IPS InLine supplied by Ivoclar Vivadent Company, Liechtenstein) has been added to the solution in three weight concentrations (70%, 80%, and 90% porcelain), while maintaining the mixing process with magnetic stirrer during gelation process for about 2-3 hours until the gelatin was completed. The mixing process should be continued to prevent precipitation of the porcelain particles and ensure mixing all the components homogenously. After that condensation method to prepare all specimens was made according to ISO 6872[31] by mixing the ceramic powder with distilled water (molding liquid) with liquid to powder weight ratio 0.335 and then pour the mixture in a steel mold. To homogenize disrupt the mixture and remove the excessed liquid and compact the powder, a vibrator with vibration for 90 sec was used. The molded samples were dried by using a filter paper for many times. After making sure that the sample dried completely we take out the sample by hand pressure. Then, the samples were sintered in the furnace (VITA VACUMAT 6000 M) through a firing cycle as mentioned in the manufacturer’s instructions of dental porcelain [32], Table (1) shows firing cycle of the samples.
Table 1: Firing cycle of the samples according to manufactures instructions [32].

| Tmax (°C)  | 950 |
|----------|-----|
| Heating rate °C / min | 60 |
| Stand by temperature °C | 403 |
| Drying time (min) | 4 |
| Vacuum start °C | 450 |
| Vacuum release °C | 949 |
| Holding time (min) | 1 |

2.1.3. Simulated body fluid (SBF) solution

To study the in vitro bioactive properties of the fabricated biocomposites, SBF should be used. The inorganic ions concentrations in SBF are similar to that existing in the blood plasma as listed in Table (2). Frequently, to accelerate the formation of the apatite layer on the material surface [33], a concentrated form of simulated body fluid is used. However, the concentrated SBF contains ions with concentrations 1.5 times that of conventional SBF [33,34]. 1.5SBF works on increasing the degree of supersaturation while maintaining the ratio of Ca to P [33].

The simulated body fluid (SBF) is prepared as published by Kokubo and Takadama [34]. All materials that involved in the preparation of the SBF and 1.5SBF were weighed by the sensitive balance with accuracy (± 0.0001%). The weights of the reagents are listed in Table (3). The procedures to prepare 2000 ml of SBF can be described as following:

1-First of all, 1400 ml of deionized water have been put in a glass beaker 2000 ml on a hot plate stirrer. After heating the water to the required temperature, the heated water was transferred to a baker plastic and covered with plastic film, while continuing in mixing during the preparation process.

2-The reagents from 1st to 8th one was added consequently to the solution with making sure that each material added is completely dissolved before adding the next material.

3-The next step was adding drops of the 9th and 10th reagents (Tris and 1M-HCl) little by little alternatively until the pH of the final solution became 7.4 at temperature 36.5 ± 0.5°C.

4-The pH of the solution finally has been adjusted to 7.4 exactly at 36.5 °C. The prepared solution was transferred from the beaker to polyethylene bottles and kept at room temperature until its temperatures were about 20 °C. After cooling, the distilled water was added up to the total capacity of the beaker (2000ml).

5-The CaSiO₃ and composite specimens were soaked in SBF at room temperature for 4, 8, 16 and, 32 days. Before doing the test, the specimens were rinsed with ethanol and water and dried at 70 °C for (6-8) hr. To provide constant chemical composition of solution, the simulated body fluid was changed every 4 days.

The bioactivity of the ceramic powder was investigated through XRD and SEM-EDS tests by soaking 600mg of CaSiO₃ powder that sintered at 700 °C in 1000 ml SBF and by soaking the prepared sample which was sintered at 950 °C in 100 ml 1.5 SBF. It is important to notice that the glass containers should be avoided, because apatite nucleation can be induced at the surface of a glass container [34].
Table 2: Ionic concentrations of different solutions (mol/m$^3$) [34].

| Ion concentrations (Mm) | Na$^+$ | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ | Cl$^-$ | H(CO$_3^-$) | H(PO$_4^{2-}$) | ($SO_4^{2-}$) | pH |
|-------------------------|-------|------|---------|---------|------|----------|----------|----------|-----|
| Blood plasma            | 142   | 5    | 1.5     | 2.5     | 103  | 27       | 1        | 0.5      | 7.2-7.4 |
| SBF                     | 142   | 5    | 1.5     | 2.5     | 147.8| 4.2      | 1        | 0.5      | 7.4  |

Table 3: Reagents required for preparation of SBF and 1.5 x SBF solution [34].

| Seq. | Reagents | SBF in 1 liter | SBF in 2 liter | 1.5*SBF in 1 liter | 1.5*SBF in 2 liter |
|------|----------|----------------|----------------|--------------------|--------------------|
| 1    | NaCl     | 8.035 g        | 16.07 g        | 12.053 g           | 24.105 g           |
| 2    | NaHCO$_3$| 0.355 g        | 0.71 g         | 0.533 g            | 1.065 g            |
| 3    | KCl      | 0.225 g        | 0.45 g         | 0.338 g            | 0.675 g            |
| 4    | K$_2$HPO$_4$3H$_2$O | 0.231 g | 0.462 g | 0.347 g | 0.693 g |
| 5    | MgCl$_2$6H$_2$O | 0.311 g | 0.622 g | 0.467 g | 0.933 g |
| 6    | 1M HCl   | 39 g           | 78 g           | 56.5 ml            | 117 g              |
| 7    | CaCl$_2$ | 0.292 g        | 0.584 g        | 0.438 g            | 0.876 g            |
| 8    | Na$_2$SO$_4$ | 0.072 g | 0.144 g | 0.113 g | 0.216 g |
| 9    | Tris     | 6.118 g        | 12.236 g       | 9.177 g            | 18.354 g           |
| 10   | 1M HCl   | 0-5 ml         | 0-10 ml        | 0.75 ml            | 0-15 ml            |

2.1.4. Analytical Methods for Characterization

The pure and composites prepared samples, before and/or after soaking in SBF, were characterized by many analytical methods. In order to characterize the crystalline structure of the prepared samples before and after dipping in SBF solution, XRD (6000 SHIMADZU X-Ray diffractometer, Japan). Microstructure, morphology and chemical compositions of the prepared sample were examined using scanning electron microscopy (inspect S50 SEM, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX) system.

3. Results and Discussion

XRD was performed before soaking in SBF to characterize the crystalline structure of bioceramics that used in this work. Fig. (1a, b) shows the x ray diffraction pattern of CaSiO$_3$ powder heat treated at 700 °C and 950 °C. From Figure (1a), one can see that the amorphous phase is predominant in this spectrum which refers to there is no phase and it is to written as below of amorphous structure. No peaks indicate to the crystalline phase, either α or β-wollastonite CaSiO$_3$. XRD results of amorphous CaSiO$_3$ agree with the results of many publications where the researchers prepared CaSiO$_3$ bioceramics by by sol-gel rout under the same thermal treatment conditions [35,36].

However, Fig.(1b) Fig.(1b) presented many peaks of new phase, it was the crystalline phase of the calcium silicate ceramics.

Thermal treatment of CaSiO$_3$ at 950°C lead to transform of the amorphous phase to the crystalline structure. The crystalline form pseudowollastonite($α$-CaSiO$_3$) are identified by the peaks at 2θ = 25.89°, 27.47°,31.73°, 36.45°, 45.29°, 45.71°, 46.09°, 49.57°,54.2°, 56.79° that can be assigned, respectively, to the (−210), (112), (−222), (008), (−218), (−300), (031), (119), (−422) and (−424) planes of $α$-CaSiO$_3$ phase according to the XRD card (00-031-0300). Other small peak at 2θ = 22.13°, 45.01° that can be assigned, respectively, to the (101) and (202) planes may be belonged to the calcium silicate(Ca$_2$SiO$_4$) phase according to the card (00-052-0069). These results are in agreement with that reported by Julian, et al [37] and Chun-Cheng, et al [38].
Figure 1: The X-radiation spectrum of CaSiO$_3$ powder heat treated (a) At 700 °C (b) At 950 °C.

Fig. (2) displays the XRD pattern of the dental ceramic (porcelain) that have been used in this study. Numbers of peaks have been appeared on a wide background. These peaks represent the reflections of X-radiation from the tetragonal Leucite phase (KAlSiO$_3$O$_6$) where their positions at 2θ = 16.38º, 25.95º, 27.18º, 30.48º, 31.46º, 33.6º and 38º that can be assigned, respectively, to the (211), (004), (400), (420), (323), (314) and (404) reflections of leucite phase according to the XRD card (00-038-1423). The same results have been obtained by the Refs. [39, 40, 41].

Figure 2: The XRD pattern of the dental ceramic (porcelain).

Because, in practice, porcelain needs to be treated thermally (sintered) at a temperature of 950 °C to form a solid material suitable for the work of the teeth restorative materials, so the crystalline structure of the Porcelain- Calcium Silicate composites should be investigated when treated at this temperature. Fig. (3) represents the XRD spectra of pure porcelain and the three composites that were studied in this research. Peaks at diffraction angles 16.9º, 26.44º, 30.91º, 31.77º, 34.22º and 38.51º are attributed to existence of leucite (KAlSiO$_3$O$_6$) crystals within pure porcelain and porcelain composite, overlapping on an amorphous background.

One can observe that increasing of CS bioceramic content in the composites leads to gradually disappearing of leucite effect and appearing new additive peaks with high intensities. These new x-ray reflections at 27.7º and 46.21º 2θ may be belonging to the (-122) and (031) reflected planes of α-CaSiO$_3$ that crystallized as a result to the high temperature of sintering (950°C). Also, two major reflections at 22º and 45.56º of the calcium silicate (Ca$_2$SiO$_4$) phase according to the card (00-052-0069) have been seen in the pattern.
XRD spectra of CaSiO$_3$ bioceramics in the powder form with different immersion time in SBF; 8, 16 and 32 days, have been displayed in Fig. (4). As can be seen in 8 day, major peaks reflections at 25.83º, 28º, 31.66º, 34.31º, 39.53º, 46.5º, 49.4º and 53.15º in 2θ, and in 16 day, major peaks at 25.86º, 28º, 31.96º, 34.45º, 39.64º, 46.61º, 49.53º and 53.22º in 2θ, and in 32 day, major peaks reflections at 25.86º, 28º, 31.95º, 34.47º, 39.67º, 46.62º, 49.44º and 53.21º in 2θ, that can be assigned, respectively, to the (002), (102), (211), (202), (310), (222), (320), (004) reflections of HAP according to ASTM card [JCPDS pattern NO. 09-0432] which are indicated to the "formation of calcium phosphate" crystals on the surface of the sample, overlapping on a random background.

This result is in a good agreement with that published by Xanthippi et. al.in Ref. [42]. Salinas et. al. [36] and Yong Kim et. al. [43]. Hydroxyapatite; HAP (calcium phosphate phase) is formed as a result to the chemical interaction between the Ca$^{+2}$ and P$^{+4}$ ions that are present in SBF with the Ca$^{+2}$ that solute from CaSiO$_3$ in the solution. However, it can be observed that increasing of immersion time lead to form more HAP crystals which indicated by increasing the reflected X-ray intensity. However, in order to investigate the bioactivity of the composite ceramic of sintered bulk sample, the composite with the largest amount of CaSiO$_3$ have been chosen to test through XRD technique. In spite of the low concentration of CaSiO$_3$ in the P70CS30 composites, but the bioactive effect was very clear. This result may be due to the effect of concentrated SBF (1.5SBF) which makes the solution saturated with the ions needed to create and accelerate the formation of apatite layer. However, no leucite peaks were
noticed. On the other side, XRD measurements of P70SC30 sol-gel sintered specimen in 950 ºC have been displayed in Fig. (5). X-ray profile revealed the formation of HAP crystals after soaking at 1.5SBF for 32 days. The bioactivity of P70SC30 bioceramics are characterized by observing peaks at 25.76º, 28.16º, 31.74º, 32.03º, 34.1º, 39.84º and 46.82º that attributed to the (002), (102), (211), (112), (202), (310), (222) and (320) reflections of HA according to ASTM card [JCPDS pattern NO. 09-0432]. These results agree with Ref. [44].

Figure 5: XRD spectra of P70CS30 composites sintered at 950 ºC immersion 32 day in 1.5 x SBF.

SEM-EDS of CaSiO₃ before and after soaking in SBF. Figures (6,7) display the (SEM-EDS) results of CaSiO₃. In Fig. (6) and Fig. (7), the morphology of CaSiO₃ particles before and after soaking in SBF for 32 days were showed respectively. A thick layer of bone-like apatite was formed on the surface of the particles. This result agrees with the XRD measurements, since peaks which indicated to the presence of hydroxyapatite material have been appeared clearly. On the other side and before soaking in SBF, EDS results indicates to the presence of O₂, Si and Ca where the CaSiO₃ are original composed as shown in Fig.(6b). In Fig.(7b) after immersion for 32 days, appearance of phosphate traces has been detected clearly. Also, Ca content increased drastically in comparison with a significant decrease in Si concentration. The total elimination of Si from the substrate indicated the precipitation of a thick hydroxyapatite layer on the surface of the grains which the Ca/P ratio by EDS is 1.409 this result is in agreement with that reported in Ref [45].

The microstructure and the morphology surface of P70CS30 bulk specimens (at 950 ºC) before and after soaking in 1.5SBF was investigated with (SEM) as show in Fig. (8) and Fig. (9). After 32 days of soaking, in Fig.(9a) show an appetite aggregation have been noticed to be crystallized on the surface ceramics particles and formed a non-uniform layer of hydroxyapatite. Fig.(8b) and Fig.(9b) displayed the chemical composition of elements in P70CS30 sintered specimens before and after immersion in 1.5 SBF respectively. Ca/P ratio by EDS was 1.694 very close to the ratio of HAP bone in which stoichiometric hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is (Ca/P=1.67).

Figure 6: SEM-EDS measurements powdered CaSiO₃: (a) SEM and b) EDS before immersion in SBF.
Figure 7: SEM-EDS measurements powdered CaSiO$_3$: (a,) SEM and (b) EDS after immersion in SBF for 32 day.

Figure 8: SEM-EDS measurements sintered specimen P70CS30: (a) SEM and (b) EDS before immersion in 1.5SBF.

Figure 9: SEM-EDS measurements sintered specimen P70CS30: (a) SEM and (b) EDS after immersion in 1.5SBF for 32 day.

4. Conclusion

The conclusions that can be drawn from this work are summarized as following:

1. CaSiO$_3$ showed a better bioactivity in comparison with its composites and increasing bioactivity with increasing immersion time in SBF.
2. Heat treatment temperature has an effect on the crystallization phases of CaSiO$_3$ bioceramic and its composites. However, sintering at 950°C resulted in appearance of pseudowollastonite ($\alpha$-CaSiO$_3$) crystalline phase and calcium silicate (Ca$_2$SiO$_4$) phase.

3. The closest value to the stoichiometric hydroxyapatite, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ has been observed with P70CS30 sintered specimen where Ca/P was 1.694.

4. The composite porcelain-CaSiO$_3$ can exhibit integrity bioactivity and consequently, can be potentially used in restorative dentistry.

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