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Mechanical Properties of Porcelain-CaSiO₃ Biocomposites Prepared by Sol-Gel Method for Dental Application

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Abstract. In this study, improving the mechanical properties of Porcelain-CaSiO₃ bioactive composites has been investigated by X-ray diffraction (XRD), flexural strength, and Vickers microhardness tester. Preparing the porcelain-CaSiO₃ composite has been done using the sol-gel method from Si(OC₂H₅)₄, Ca (NO₃)₂·4H₂O as starting materials and HNO₃ used as a catalyst and mixed the sol of CaSiO₃ with Porcelain IPS inline powder with three different weight percentages of CaSiO₃ (P90CS10, P80CS20 and P70CS30 wt. %). 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 appeared. Concerning the mechanical properties, flexural strength, and Vickers microhardness for porcelain-CaSiO₃ composites were increased with increasing CaSiO₃ content in the composites. The maximum values of flexural strength and Vicker microhardness were recorded at P70CS30, and they were 99.85 MPa and 1604 MPa, respectively.

Keywords. Bioactive ceramics, Calcium silicate, Porcelain, sol-gel, Flexural strength, Vickers hardness.

1. Introduction

Bioceramics are defined as a compound of metallic materials, such as calcium, potassium, and zirconium, and nonmetallic materials, such as silicon, oxygen, and fluorine. They could be fabricated in different forms such as powder, coating, and bulk to be suitable for different applications like biological reconstruction or replacement. Bioceramics are characterized by their biocompatibility with the biological environment and their ability to integrate with hard tissues; this is due to the similarity of the chemical composition of these materials with that of bone or teeth tissues [1]. These properties made the bioceramics potential biomaterials for the regeneration of bone and restoration of dental applications [2]. However, as far as dental restorative materials are concerned, the characteristic of biological activity varies from one substance to another. In general, all dental materials should be biocompatible, harmless, no toxic, having good mechanical properties to tolerate the loads that are applied to the tooth as a result of the jaws movement, but not all of them are biologically active [3,4]. Bioactive ceramics are considered to be osteoconductive materials in which indicate the characteristic of growth the bone and bonding along the surface of the bioceramic material[2]. Bioactive glasses are known by their low mechanical properties, which limits their medical applications to non-loading bearing situations. On the other side, the bioactive glass-ceramics are the same glassy one but with improved mechanical properties by controlling the crystallization of the glass structure [5]. In 1970,



the first silicate ceramic system in the form of $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ glass was prepared by Hench et al. [6]. The Sol-gel process offers an alternative route to fabricate bioceramics. This strategy is based on the bottom-up approach by the existence of a medium under certain conditions that allow the interaction of the elementary materials to pass through several successive reactions, hydrolysis, and condensation processes to the formation of bioceramics in the nano-scale. This method includes synthesizing the ceramics by preparing a solution of chemical precursors as a starting material and followed by aging at relatively low temperatures, drying, and then applying several heat treatments to get a chemically stabilized material [7]. The main advantages of the sol-gel method are its low manufacturing temperatures [8], purity, homogeneity, and the possibility to produce different compositions with various forms such as thin films and fibers [9]. To use material as a biomedical material in contact with the cellular liquid, it must have several strict restrictions. First of all, it must be biocompatible, which means it should not negatively affect the body [10]. Also, it must be nontoxic, noncarcinogenic, nonallergic, and non-inflammatory [11]. However, biomaterial must be with sufficient strength and wear resistance that makes it suitable for the required mechanical properties of the concerned application [12]. Depending on the heat treatment (temperature of sintering through fabrication process), CaSiO_3 (CS) may be crystallized into two types; amorphous and crystalline ceramics. The amorphous CS ceramic has a glassy structure with different concentrations of CaO, where the molecules are disordered and random. The stability of this glassy structure is due to the ionic and covalent bonds that make silica units link together with a chain configuration to form the tetrahedral network. The second phase is the crystalline CS ceramics, where the molecules are arranged in an ordered manner. It may consist of: wollastonite ($\beta\text{-CaSiO}_3$), pseudowollastonite ($\alpha\text{-CaSiO}_3$), dicalcium silicate (Ca_2SiO_4), and tricalcium silicate (Ca_3SiO_5) [13]. They are porcelains with structure contains silica network (or quartz) and feldspar materials; Potash feldspar ($\text{K}_2\text{O}.\text{Al}_2\text{O}_3.6\text{SiO}_2$) and/or Soda feldspar ($\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.6\text{SiO}_2$). The benefit of adding the feldspars to the glassy silica is to form a crystalline structure of Lucite (by heat treating) to improve the mechanical properties of ceramics [14]. Increasing the amount of crystalline phase makes the ceramic material be stronger, more flexural strength with less abrasive. These materials can be used for veneer metal-crown porcelain restoration [15]. However, using Porcelain as a 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 caries [3,16]. So, the need to improve dental ceramic materials performance has become necessary. One of the approaches to achieve this goal is the fabrication of a composite of dental ceramic/bioactive ceramic that combines the required mechanical and biological qualities [17]. This study aims to fabricate a novel composite of Porcelain with different ratios of calcium silicate bioactive ceramic by the sol-gel method to enhance the mechanical properties.

2. Experimental part

Porcelain- CaSiO_3 composites samples have been prepared with different weight ratios (P90SC10, P80SC20, and P70SC30) by mixing the CaSiO_3 (80% SiO_2 -20% CaO) bioactive ceramic with traditional Porcelain (P) (IPS InLine supplied by Ivoclar Vivadent Company, Liechtenstein) by sol-gel method initially the sol was prepared by using a magnetic stirrer, to mix 25ml TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) (China, 99.0% purity) in a solution of 3.05ml nitric acid (Mumbai, India, 71% purity) (2M) and 15.8ml H_2O . After 1hr, the amount of 6.48g of $\text{Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$ (Mumbai, India, 99.0% purity) was added to the mixture with continuous mixing for 4hr. After that, the Porcelain has been added to the solution in three weight concentrations (70%, 80%, and 90% porcelain) while maintaining the mixing process with a magnetic stirrer during the gelation process for about 2-3 hours until the gelatin is completed. The mixing process should be continued to prevent precipitation of the porcelain particles and ensure mixing all the components homogeneously. The mixture was left in a closed container for three days at room temperature to form a transparent gel mass, and the resultant gel was transferred to a furnace at 70°C to work aging for three days. In this step, the size of the gel is decreased and wholly transformed into a solid phase. The solid samples were placed in the oven for drying for two days at 150°C then ground using pestle and mortar to form a powder. To nitrate elimination and stabilization, the powder heat-treated at 700°C for 3hr in an electrical resistance furnace with a heating rate of 13

°C/min and then left in the furnace to cool to room temperature. In this step, the weight of the produced powder was 8.25g. In the final step of the preparation process, the resultant materials were grinded using pestle and mortar and then sieved by a planetary ball mill (SMF-Disk-Top Planetary Ball Miller) for 30min with a milling speed of 2700rpm to obtain a ceramic powder with particle size $> 63\mu\text{m}$. After that, the condensation method was used to prepare all specimens, which were made according to ISO 6872^[18] 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 homogeneity disrupt the mixture and remove the excessed liquid and compact the powder, a vibrator was utilized to vibrate the mixture for 90 sec. The molded samples were dried by using a filter paper for many times. After making sure that the samples are dried completely, they are taken out by hand pressure. Then, the samples were sintered in a furnace (VITA VACUMAT 6000 M) through a firing cycle, as mentioned in the manufacturer's instructions of dental Porcelain^[19], Table(1).

Table 1. Firing cycle of the samples according to manufactures instructions^[19].

T max(°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

The prepared samples of pure and composites were characterized by using XRD . To characterize the crystalline structure of the prepared samples, XRD (6000 SHIMADZU X-Ray diffractometer, Japan) was utilized.

The mechanical properties of the prepared porcelain-CaSiO₃ composite were measured. The hardness test was carried out according to ASTM C-1327^[20]. In this measurement, a small pyramidal diamond has been used to press into the material being tested. The test applied using Micro Vickers Hardness Tester (TH-717). The Vickers hardness number (HV) is the ratio of the applied force to the surface area of the indentation. Three samples were used in this test; for each sample, three indentions at different places were made. The applied load was 0.245N for 10 seconds. This load was chosen after continuously applied different loads until obtaining indentation without any crack. Vickers hardness was calculated by the following equation^[21]:

$$\text{HVN} = 1.8544 P/d_{av}^2 \quad (1)$$

Where:

HVN: is the Vickers hardness number, (MPa)

P: applied force, (N)

d_{av} : is the mean length of the diagonals of the indentation (mm).

The flexural strength was determined according to the ISO 6872^[18] using a three-point loading simple beam. Rectangular specimens were fabricated with dimensions of 4x3 mm for the width and height of the specimen. The distance between the support points was 40 mm, and the span length was 50 mm. The cross-head speed was 0.5mm/min; the test was performed using the microcomputer controlled electronic universal testing machine (WDW-5E, china made). Flexural strength was calculated by the following equation^[18]:

$$\sigma = 3Pl / 2wb^2 \quad (2)$$

Where:

P: Breaking load (N)

L: Distance between support rollers, (mm)

w: Width of the specimen (mm).

b: Thickness of specimen (mm).

3. Results and discussion

Figure (1) and Figure (2) show the particle size distribution of the prepared powder of CS and P70CS30, heated at 700 °C and ground by a planetary ball mill for 30 min. The obtained results were between 3.015 µm and 63.19 µm and between 2.621 µm and 56.70 µm with D50 (24.16 µm and 22.39 µm) for CS and P70CS30, respectively. The fact that the CS material is highly agglomerated so not obtained on particle sizes similar for Porcelain or lower to increasing in improving the mechanical properties of porcelain-CS composite and from these results can be concluded that the prepared powders have a wide range of size distribution.

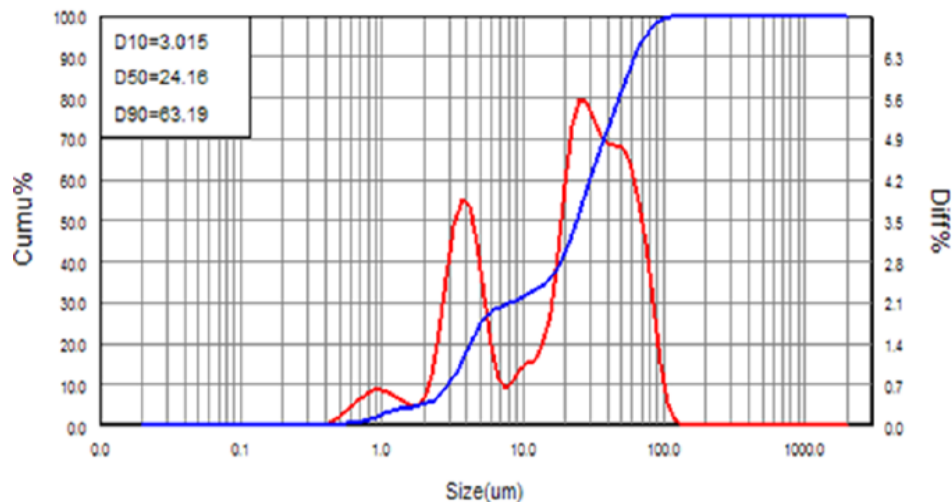


Figure 1. The particle size of CS treat powder at 700 °C ground by a planetary ball mill for 30 min.

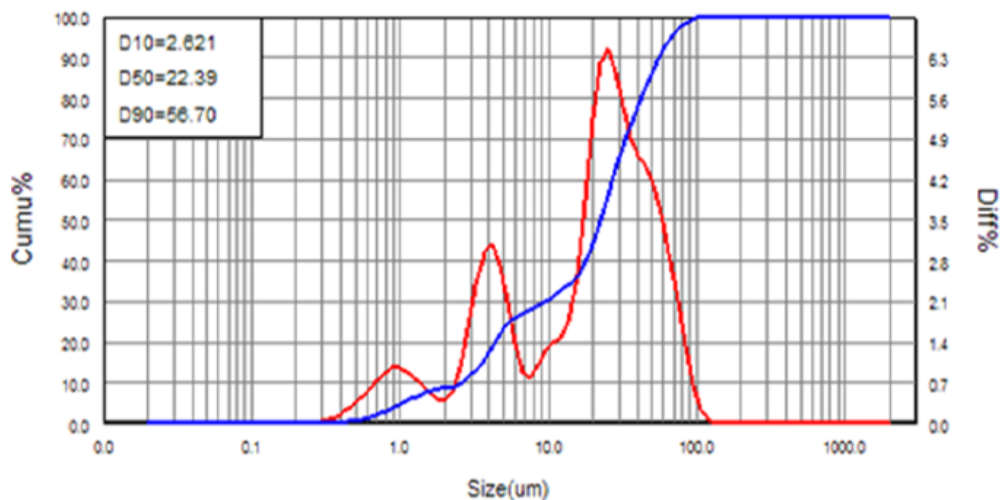


Figure 2. The particle size of P70CS30 treat powder at 700 °C ground by a planetary ball mill for 30 min.

In practice, Porcelain needs to be treated thermally (sintered) at a temperature of 950 °C to form a solid material suitable to be used as teeth restorative materials, so the crystalline structure of the P-CS composites should be investigated when treated at this temperature. Figure (3) represents the XRD spectra of pure Porcelain and the three composites studied in this research. Peaks at diffraction angles of 16.9°, 26.44°, 30.91°, 31.77°, 34.22°, and 38.51° are attributed to the existence of leucite (KAlSi_2O_6) crystals within pure porcelain and porcelain composite, overlapping on an amorphous background.

It can be observed that increasing CS bioceramic content in the composites leads to gradually eliminating the leucite effect and leads to appearing new additive peaks with high intensities. These new x-ray reflections at 27.7° and 46.21° 2θ maybe belonged to the -122 and 031 reflected planes of α - CaSiO_3 that crystallized as a result of the high temperature of sintering (950°C). Two primary reflections at 22° and 45.56° of the calcium silicate (Ca_2SiO_4) phase, according to the card (00-052-0069) have been seen in the pattern.

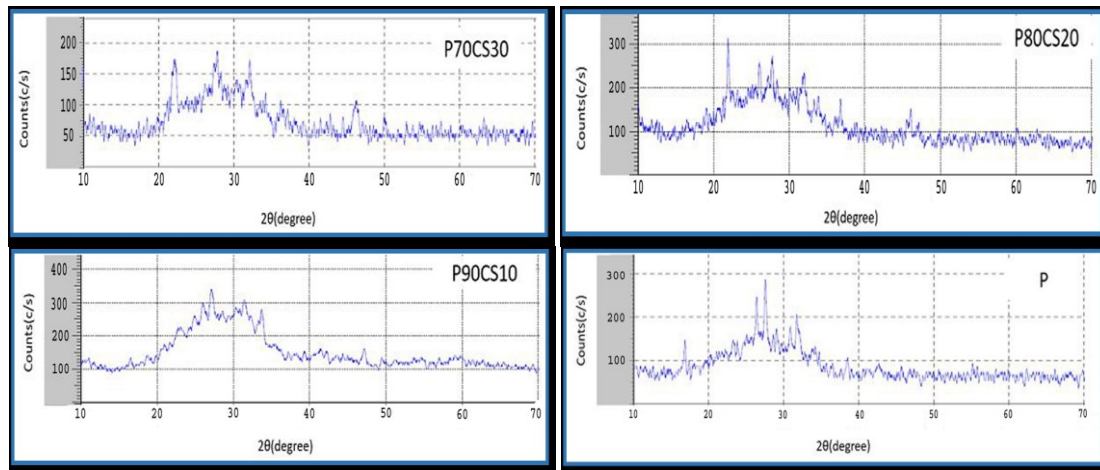


Figure 3. XRD Spectra of pure Porcelain and the porcelain- CaSiO_3 composites sintered at 950°C .

Figure (4) shows the increase the Vicker's microhardness of porcelain composite with increasing calcium silicate CaSiO_3 wt.% content. The results show a linear increase in the Vicker's microhardness of composite with the increase in the CaSiO_3 wt.%. The porcelain- CaSiO_3 bioactive composites (P90CS10, P80CS20, and P70CS30) exhibited a higher value of microhardness at 1604 MPa compared to porcelain material at 885.98MPa. The higher value of Vicker's microhardness for the experimental porcelain- CaSiO_3 bioactive composites is possibly due to the existence of various crystalline phases within the glass structure^[22]. Moreover, the results of X-ray (Figure1) clearly show that the pure porcelain maturity by the forming of leucite crystals (KAlSi_2O_6) and in the case composite porcelain- CaSiO_3 where it was obtained, two more crystalline phases are developed, which are wollastonite (CaSiO_3) and calcium silicate (Ca_2SiO_4); however, crystallinity has improved the mechanical properties of the ceramic composite. Somehow or other, the crystals blended with the glassy matrix on ceramic will have higher hardness with increasing the content of the calcium silicate CaSiO_3 wt. %. Those raw materials take place on determining Porcelain's characteristics. The recorded values of microhardness for porcelain and porcelain composite were in a good agreement with results reported in the literature^[23,24, 25, and 26].

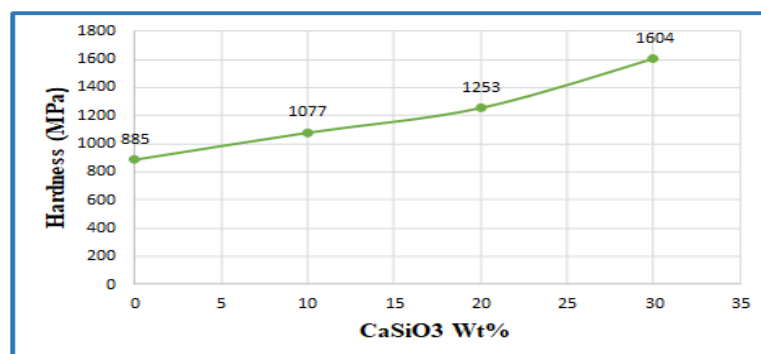


Figure 4. Schematic representation of the relation between Vicker's microhardness and porcelain composite (CaSiO_3 wt.%).

Figure (5) shows the average flexural strength for pure Porcelain (P) and Porcelain- CaSiO_3 bioactive composites (P90CS10), (P80CS20), and (P70CS30). The results of the average flexural strength obtained from the three-point bending tests show 104 MPa for pure Porcelain and 99.85 MPa for P70CS30, respectively. Where it was obtained, the pure Porcelain has the highest average flexural strength at 104 MPa, and the flexural strength had decreased in Porcelain when it was combined with bioactive glass CaSiO_3 . In the case of P70CS30 (99.85), it was observed that the flexural strength value near the pure Porcelain (104 MPa) and this is a very good result obtained for bioactive composite. This result is in agreement with that reported in Ref. [3]. Values obtained through the three bending tests (104 MPa) for pure Porcelain are agreed with the range of flexural strength for Porcelain (IPS InLine), according to the manufacturer, which has the flexural strength of 80 ± 20 MPa. However, it could not get good results with Porcelain - CaSiO_3 bioactive composites (P90CS10), (P80CS20).

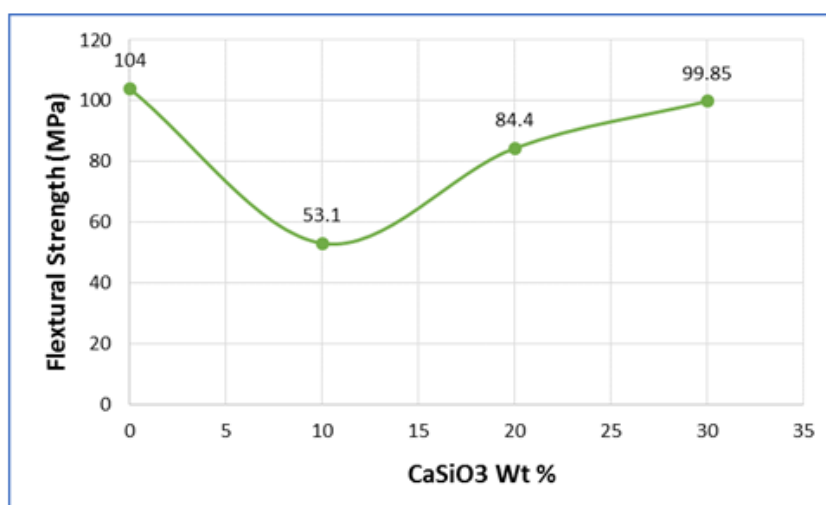


Figure 5. Schematic representation of the relation between flexural strength and porcelain composite (CaSiO_3 wt. %).

4. Conclusion

Heat treatment temperature affects the crystallization phases of porcelain- CaSiO_3 composites. From XRD patterns, sintering at 950°C resulted in the appearance of pseudowollastonite ($\alpha\text{-CaSiO}_3$) crystalline phase and calcium silicate (Ca_2SiO_4) phase. This leads to improving the mechanical properties of the porcelain- CaSiO_3 composites with increasing CaSiO_3 concentration. In conclusion, composite porcelain- CaSiO_3 can exhibit good mechanical properties that can be potentially used in restorative dentistry.

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