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Preparation of Hydroxyapatite/ Zirconia Porous Composites via Polymeric Sponge Method and Study the Physical and Bioactivity Properties

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Abstract. In this study, Hydroxyapatite/ Zirconia porous composites at different ratio were fabricated by polymeric sponge method. HAp were produced via solid state reaction in molar ratio (3:2) between TCP and $\text{Ca}(\text{OH})_2$. The crystal structure of the samples were characterized using X-ray diffractometer (XRD), scanning electron microscopy (SEM). Furthermore, the porosity and rheological properties of the samples were also tested. It's found that the compression strength with the highest value (13.2 MPa) obtained when the composition ratio is (30:70 wt %) and porosity (65.7%). Incubated for 30 days in Simulation Body Fluid, a bone like apatite layer was completely formed on the surface of the porous composite.

Keywords. Hydroxyapatite, Zirconium oxide, Polymeric sponge method, mechanical properties, simulation body fluids, degradation.

1. Introduction

Hydroxyapatite (HAp) ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a promising material for bone reconstruction based on its chemical structure. It is very much the same to the mineral parts of bone and tooth and shows excellent biocompatibility and osteoconductive properties [1, 2]. Additionally, HAp materials do not exhibit any cytotoxic effects [3]. Yet, the application of HAp is restricted for use as implant material because of its poor mechanical properties [4, 5]. Many studies focused at improving the mechanical properties of HAp, for example making them as composite materials [6]. Addition of second-phase ceramic materials (e.g. ZrO_2 , TiO_2 or Al_2O_3) into the HAp matrix for improving strength and toughness [7].

Zirconia (ZrO_2) is a well-known reinforcing factor as a result of it's comparatively "high mechanical strength, toughness, wear resistance, corrosion resistance and biocompatibility" [8, 9]. At ambient pressure, ZrO_2 polymorphs occur in three forms; monoclinic (M), tetragonal (T), and cubic (C) depending on the temperature [9, 10]. As a result of phase transformation, pure and single-phase ZrO_2 tends to fracture even at room temperature, leading to deterioration in mechanical properties and consequently making it unsuitable for clinical applications. Therefore,



ZrO₂- based composites possess enhanced toughness following controlled phase transformation of stabilized ZrO₂ doped with yttria (Y₂O₃) (Y-TZP) [10]. Theoretically, ZrO₂ can be utilized as a composite material because of its stable-biocompatibility and proceed superb mechanical properties [11]. Furthermore, ZrO₂ is also very appropriate to be utilized as a bone and dental implant material because of its aesthetic quality properties [12].

Many techniques have been sophisticated to manufacturing porous HAp /ZrO₂ composite scaffolds, generally including of organic particles in the HAp/ZrO₂ composite powder, direct foaming, and polymeric sponge method [13, 15]. Porous ceramic which prepared by the replication method have a “controllable pore size, interconnected pores, and desired geometry” but a weak mechanical properties for using in load-bearing [16].

Previous studies focusing on the use of other materials to form HAp composites which have better compressive strength. Wang et al. studied 3%yttria-stabilized 20wt% zirconia (ZrO₂) to get porosity between (87%~35%) and a compressive strength of (12 MPa) [17].

Here, we report on zirconium oxide (ZrO₂) particles that used for reinforcing hydroxyapatite particles for orthopedic implant considerations. Specifically, the effects of ZrO₂ particle on bioactivity property of hydroxyapatite for bone regeneration. The porosity and viscosity were determined by Archimedes method and viscometer at spindle speed of (100 rpm). The Crystallographic & morphological studies were performed using optical micrograph, X- Ray diffraction and “Scanning electron microscope”, compression strength of the templates were tested by compression strength test “ASTM C77-88 (1999)” using Instron machine “model 1195” at crosshead speed of (1 mm/min).

2. Experimental Procedure

2.1 Preparation of the Samples

The fabrication of high porous HAp/ ZrO₂ biocompatibility ceramic foam was done. Initially HAp powder was fabricated by solid state synthesis the starting material that have been used were commercial tricalcium phosphate TCP (Himedia, India) and calcium hydroxide, Ca(OH)₂ (Himedia, India). The powders mixed in 3:2 molar ratio and were mechanically dispersed in de-ionized water at solid loading 55%. Thereafter adding 3% yttria-stabilized zirconia with ratios of (5, 10, 15, 20 and 25 wt%) from the total solid loading , loaded and 4% (poly vinyl alcohol); PVA were added as a binder and magnetic stirred for 2 hours until the PVA dissolve and the slurry with (pH= 12) is ready for the dipping process .

Polymeric sponges that used each cut into a dimension of 1 cm³. The viscosity of the ceramic slurry was analyzed utilizing viscometer. The templates were squeezed by hand many times then put in a “desiccator” and evacuated to (10⁻¹ bar) to take off the restricted air and make certain that the templates are fully filled with the ceramic slurry. The excess ceramic slurry was extracted by squeezing the sponge through a roller. The filled samples were dried in “microwave oven” for (10 to 25 minute) according to viscosity of solid loading. The Samples were sintered at 1250 °C with heating rate of 5 °C/min and three hours of soaking time.

2.2 Immersion in SBF Solutions

Samples (HAp+ ZrO₂ porous composites) (1 cm³) were put in plastic containers with (500 ml) of (SBF x5 gm/l). The containers were sealed with an airtight and the temperature stay constant at 37 °C. After (30 days) in touch with SBF to perform many characterizations rinsing them with distilled water and then drying them with microwave to prepared it for XRD and SEM analysis. Table (1) shows the composition of simulation body fluids.

Table 1. Composition of SBF and concentration of (SBF×5) [17].

ITEM	SBF×5 (gm/l)
NaCl	40.18
NaHCO ₃	1.76
KCl	1.125
K ₂ HPO ₄	1.15
MgCl ₂ .6H ₂ O	1.555
CaCl ₂	1.465
NaSO ₄	0.36

3. Results and Discussion

3.1 Morphological Characterization

Representative SEM and optical pictures of HAp/ZrO₂ samples sintered at 1250°C are respectively showed in Fig (1). As the HAp/ZrO₂ concentration was “increased”, the pores became “interconnected with more dense and thicker pore walls”, which are very important factors that enhancing the mechanical properties of the porous materials.

At low concentration of HAp/ZrO₂ which is (35%), the “polyurethane foam structure” was completely replicated with fully interconnected open pores. Yet, when the HAp/ZrO₂

concentration reached to (55%), the pores were slightly blocked as an effect of thicker walls. A elevated densification regime is indicated after sintering at (1250 °C) which showed that the sintering process almost complete and subsequently grain growth occurred at temperature (1250°C) with minimum decomposing of HAp to Tri calcium phosphate.

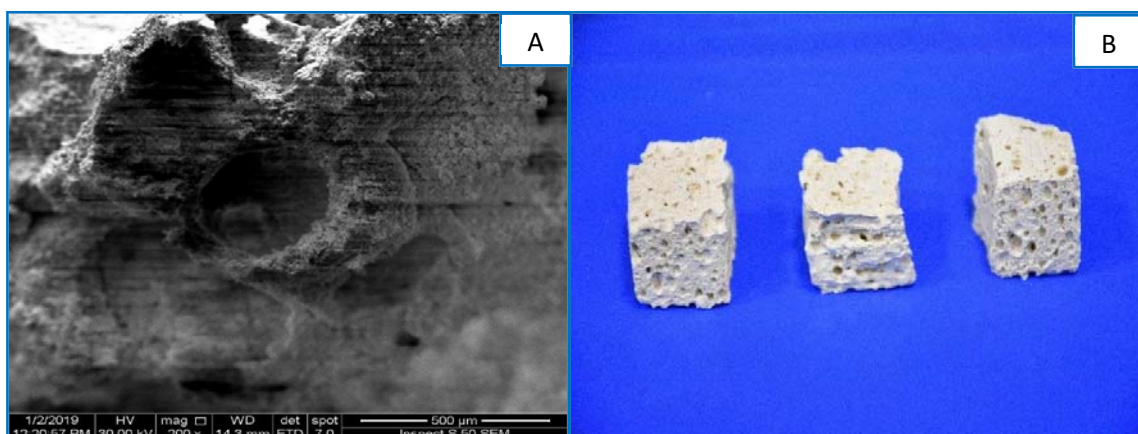
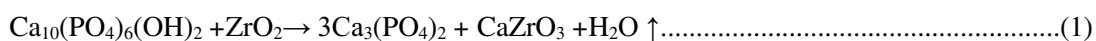


Figure (1). A. SEM image of hydroxyapatite/ZrO₂ porous ceramic sintered at 1250 °C, B. Optical micrograph of ceramic composites foam.

3.2 Crystallographic Investigation

The results of the crystallographic analysis of the produced samples, carried out with “X-ray diffraction”, are presented in Fig. 2. X-ray diffraction patterns of HAp/ZrO₂ composite samples reveal peaks associated with HAp (Card no. 01-074-977). From the XRD it can be seen that at temperatures of (1250 °C), a continued shrinkage in the yield of HAp phase and an increased yield of (b-TCP) is can be seen. HAp is decomposed by heat into (b-TCP), (Ca₃(PO₄)₂), (CaZrO₃) and (water vapor). The (CaZrO₃) released stabilizes the (m-ZrO₂) by solid solution which create the formation of (t-ZrO₂). This is lead to the fact that “porous HA/ZrO₂ scaffolds” have a better mechanical properties compared with that of pure HAp porous scaffolds. The following chemical reaction is suggested:-



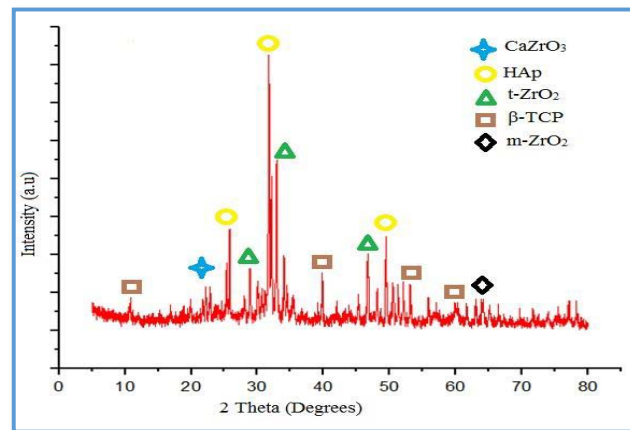


Figure (2). XRD patterns of HAp/ ZrO₂ powder.

3.3 Physical Properties Measurement

Fig.3 (A) showed the porosity over the change of the ratios of (HA/ZrO₂) samples as an action of (HA/ZrO₂) concentration. The porosity “decreased with increasing (HA-ZrO₂) concentration”. The obtained porosity ranging from (65.7 to 84.4%), are predictable to be sufficient to allow the tissue ingrowth and anchor the prosthesis to the surrounding bone in addition to provide blood and nutrients to the “bone-like vascular canals”. This behavior could be understood in term of the rheological properties where viscosity of the slurry is one of the most important factors that control the porosity. Since solid loading is responsible for open and close porosity, clearly increasing viscosity will greatly decreases the physical properties as shown in Fig.3 (B), because it will block the open porous, therefore, decreasing the solid loading usually enhances the physical properties but decreases the mechanical one [19].

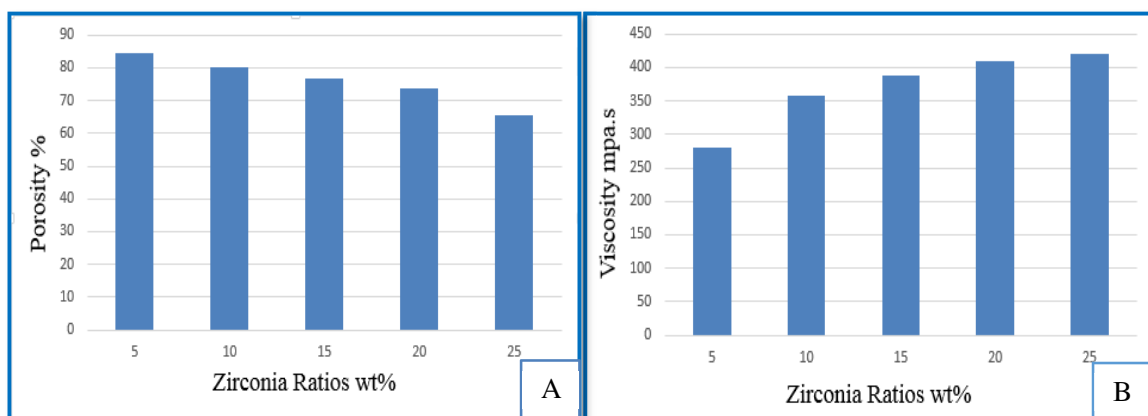


Figure (3).A. Porosity as % of hydroxyapatite /ZrO₂ porous ceramic at (5, 10, 15, 20, 25%) from total solid loadings, B. Viscosity of hydroxyapatite /ZrO₂ porous ceramic at (5, 10, 15, 20, 25%) from total solid loadings.

3.4 Compression Strength Measurement

Fig. 4 shows the compressive strength HAp composites (5, 10, 15, 20 and 30wt% ZrO_2) prepared under vacuum and dried by microwave oven. The highest value for compressive strength was obtained for samples prepared at (25 wt. %) (13.2 MPa), (20wt %) (10.1 MPa), (15wt %) (8.3 MPa), (10wt %) (6.25 MPa) and finally the lowest at (5 wt. % ZrO_2) (4.5 MPa). This was attributed to highest density, the higher result of porosity percentage contributed to lower strength of samples. This result due to cell wall thickness that increased with increasing zirconia ratio. This was mainly because of the porosities decreased as the weight fraction of the zirconia increased. The strength is a property which is strongly dependent on the porosity and microstructural defects of the samples.

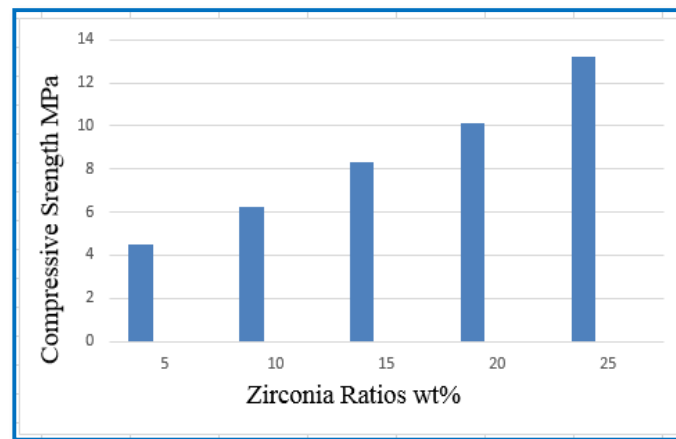


Figure (4). Compressive strength of hydroxyapatite / ZrO_2 at (5, 10, 15, 20, 25 wt. %) from total solid loadings.

3.5 Bioactivity Tests

In order to investigate the bioactivity behavior of the specimens and, in vitro test was carry out. In (vitro test) was carried out in “simulated body fluid (SBF)”, prepared according to the “Kokubo prescription” [20, 21] under a stable temperature (37 °C) and pH (7.2). Templets were extracted from the solution after (4 weeks). Bioactivity tests were done on the templates which showed highest physical and mechanical properties. Starting from the first week, intensive “apatite layer” formation for all samples were determined as shown in Fig. 5 which show the SEM image. When the immersion period in SBF was “increased”, the “size and quantity of the apatite layer” increased, too, as predictable. Unexpectedly, the size and quantity of the apatite layer also increased with increasing firing temperature. This is perhaps based on a quiet “smooth morphology, well-arranged grains, and presence of the glassy phase” which improving the apatite

formation at higher firing temperatures. At the end of (4 weeks), the samples' surfaces were completely covered by the "apatite layer". For the (HZC composites⁰ sintered at (1250 °C), the present apatite nucleation was seen only around ZrO₂ grains in the "first week". At the end of (3 weeks), the apatite accumulation also happen on the ZrO₂ grains.

The results in Fig. 6 of XRD analysis of sample (75% HAp + 25% ZrO₂) composites, soaked in SBF solution for 30 days and if compared between A and B its can been seen that all the peaks referred as Ca₃(PO₄)₂, CaZrO₂ are completely disappears and HAp phase had also changed and become less in height in some positions.

Also the Ca/P ratio change before the immersion was (1.67) and after (1.25) for the selected sample. This decrease may be attributing to precipitation of a non-stoichiometric HAp from SBF. This result is in a good agreement with the earlier report that had written by Kaygili et al. [22] and also agree with Bulut et al. as they stated in their paper the apatite nucleation was also observed on (ZrO₂ grains). At the end of the 'four weeks', the matrix was fully coated with an appetite layer. [23]

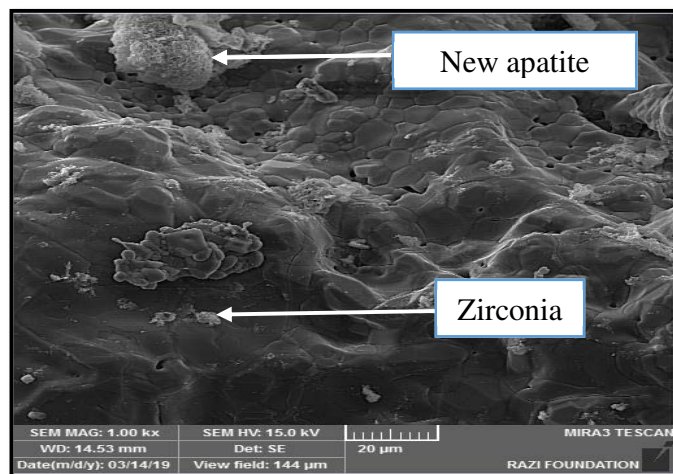


Figure (5). Scanning electron micrographs of HAp/ZrO₂ porous composites after 30 days of immersion in 5xSBF at 37 °C.

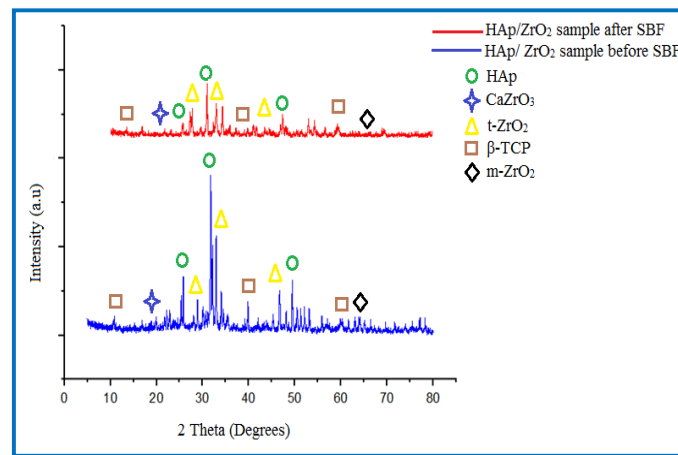


Figure (6). Show the XRD analysis before and after SBF soaking for 30 days at 37 °C.

4. Conclusion

HAp/ZrO₂ porous composites were successfully fabricated by mixing Tri Calcium Phosphate and Calcium Hydroxide in “molar ratio (3:2)” via polymeric sponge methods. The porosity in the porous ceramic can be controlled by changing (HAp/ZrO₂) concentration and the porosity is ranging (65.7- 84.4%). A compressive strength of (10.1 MPa) for (HAp/ZrO₂) porous scaffolds with (HAp/ZrO₂) concentration of (25 wt% zirconia+ 75wt% HAp) is the best because it's similar to cancellous bone, the composites having the best physical and mechanical properties also enhanced bioactive properties which is very comparable to that of cancellous bone. Overall, this study introduces a new method to create (HAp/ZrO₂) porous ceramic composites and its can be used as promised candidate for bone replacement and regeneration.

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