Microstructure, Hardness, and Electrical Conductivity of \(\beta\)-TCP/Zirconia Composites Prepared from Eggshell

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Abstract. In this research, \(\beta\)-TCP composites with zirconia at different compositions were fabricated via solid-state reaction method. \(\beta\)-TCP was produced from eggshell. The crystal structure of the as-prepared samples was characterized using X-ray diffractometer (X-RD). Meanwhile, elemental mapping and the microstructural characteristics of the samples were characterized by scanning electron microscopy (SEM). A Vickers hardness test was performed to investigate the hardness properties. In addition, the porosity and the electrical conductivity of the sample were also analyzed. The XRD data showed that \(\beta\)-TCP was successfully synthesized from the eggshell. Based on Vickers hardness test results presented the sample with 40:60 wt\% composition has a higher hardness that supported by SEM characterization that is homogeneous. Furthermore, the electrical conductivity with the highest value of 0.05470 (S cm\(^{-1}\)) showed by the sample with 30:70 wt\% composition.

Keywords. \(\beta\)-TCP/zirconia, eggshell, solid-state reaction, and physical properties.

1. Introduction

To date, the study of biomaterials has been extensively done by many researchers due to their potential applications in the field of biomedicine. Tricalcium phosphate (TCP) is one of the biomaterials which commonly used in orthopedic, dental, and plastic surgeries for healing of bone defects, fracture treatment, total joint replacement, fundamentally related replacement and regeneration of bone tissue [1]. TCP with a chemical formula of \(\text{Ca}_3(\text{PO}_4)_2\) is the bioceramic material with similar composition patterns with to human bone performing excellent biocompatibility, osteoconductivity and ensuring colonization of material by new bone, and bioactivity with surrounding living tissue [2, 3].

Among CaP-based bioceramics, \(\beta\)-TCP has excellent resorbability in a human biological environment allowing progressive replacement of the natural host tissue with gradual degradation of the implanted material to make it ideal for bone reconstruction [4, 5]. It is known that there is a trend in increasing biodegradability, osteoconductivity, and osteoinductivity when coming in contact with biological tissue [6]. \(\beta\)-TCP is stable at room temperature and the ideal Ca/P ratio is 1.5, it crystallizes in rhombohedral structure with a space group of \(R\ 3\ c\); lattice parameters of \(a = 10.4121\ \text{Å}\); \(c = 37.3517\ \text{Å}\) with Ca/P ratio similar to that of bone tissue [7]. So far, \(\beta\)-TCP has been synthesized by different routes, including wet-chemical, solid state synthesis, and microwave irradiation [8]. Meanwhile, calcium (Ca) that found in eggshells in the form of calcium carbonate (CaCO\(_3\)) with the
composition of 90.9 % [9], presenting a prominent raw material to produce β-TCP. In addition, calcium eggshells also become a useful source of bone metabolism [10]. Therefore, utilization of eggshells to produce β-TCP is important to be conducted.

In general, β-TCP has low mechanical properties and rapid biodegradation rate [11]. The main problem, at this time, is how to control the degradation rate and improve the mechanical properties of β-TCP [12–18]. Furthermore, for tissue replacement and regeneration applications, the conformity requirement between degradation rate and mechanical properties with tissue cell growth rate is then strongly required. Therefore, it is also vital to improve the mechanical properties and control the rate of β-TCP degradation. In this work, we propose the compounding β-TCP with zirconia (ZrO₂). Theoretically, ZrO₂ can be used as a composite material due to its stable-biocompatibility and performs excellent mechanical properties [19]. Moreover, ZrO₂ is also very suitable to be used as a dental implant material due to its low thermal conductivity and aesthetic quality properties [20].

Based on the above explanation, it is essential to investigate the structural and physical properties as well as crystal structure, size and morphology, hardness, and electrical conductivity of the β-TCP/ZrO₂ composites from the eggshell.

2. Materials and methods

2.1. Synthesis and characterization of bioceramics composite β-TCP/ZrO₂ from eggshell

In this study, β-TCP was prepared from a natural eggshell and composited with zirconia for obtaining a better physical property, i.e., hardness and electrical conductivity. Regarding bone graft applications, some important of the physical properties, i.e., porosity, hardness, electrical conductivity, and microstructure ware tested. The results of the composition test of an eggshell element were conducted by X-ray fluorescence (XRF). The CaO was calcined at 1000 °C for 5 h and then evaluated by X-ray diffraction (XRD) to know the crystal structure. Furthermore, 100 mL of calcined-CaO solution (1.2 M) was reacted with 100 mL of H₃PO₄ 0.8 M and stirred at 600 rpm for 5 h. The solution was deposited at room temperature for 24 h, then filtered and sintered at 1000 °C for 15 h.

Both powder β-TCP and ZrO₂ were mixed using ball milling for 2 h with β-TCP: ZrO₂ ratio 70:30; 60:40; 50:50; 40:60; 30:70 (wt%). The series of the samples were formed in a cylindrical shape with the weight of 2 g prior sintering at 900 °C for 3 h. The sintered samples were characterized by means of XRD and scanning electron microscopy (SEM). The physical properties as well as porosity, hardness, microstructure, and electrical conductivity were also investigated. The porosity test of β-TCP / ZrO₂ composites was calculated using the following Equation 1 [21]:

\[
\text{Porosity} = \left( \frac{W_{\text{b}} - W_{\text{p}}}{W_{\text{p}}} \right) \times 100\%
\]

*Wₜ*: saturated burn weight, *Wₚ*: burn weight, *Wₚ*: plastic weight.

Hardness was tested with a Vickers hardness test, while the electrical conductivity determined by measuring electrical current and voltage.

3. Results and discussion

The elemental composition of the eggshell is presented in Table 1.

| Compound | S         | Ca       | Fe       | Co       | Sr       | Er       | Yb       | Lu       |
|----------|-----------|----------|----------|----------|----------|----------|----------|----------|
| Conc     | 0.040 ±   | 98.73 ±  | 0.057 ±  | 0.064 ±  | 0.20 ±   | 0.20 ±   | 0.61 ±   | 0.090 ±  |
| Unit (%) | 0.002     | 0.06     | 0.003    | 0.001    | 0.02     | 0.01     | 0.03     | 0.001    |

Based on Table 1, Ca shows dominant composition up to 98.73 % comparing to other components. Therefore, it becomes a strong reason to be used as a primary source for synthesizing β-TCP. The diffraction pattern of CaO has a crystal structure match with AMCS9 database with the code of 96-200-1133. It implies that the chicken eggshell can be used as raw material to produce calcium phosphate [9].
Figure 1 shows the matching sintered β-TCP diffraction pattern the β-TCP model of AMCSD database. It shows that β-TCP was successfully synthesized using the calcium source from the eggshell. This result is in a good agreement with the study reported by Aisyah [22]. Selection of sintering temperatures at 1000 °C for 15 h gives an appropriate synthesis as a reported by others [23].
Figure 2 XRD patterns for the β-TCP : ZrO₂ compositions of (a) 1:1 (b) 0.8:1.2 and (c) 0.6:1.4

Table 2. Porosity, hardness and electrical conductivity of β-TCP / ZrO₂ composites

| No. | Composition β-TCP: ZrO₂ (wt%) | Porosity (%) | Average Hardness Vickers (kg:mm²) | Electrical Conductivity (σ) (S·cm⁻¹) |
|-----|-------------------------------|--------------|-----------------------------------|--------------------------------------|
| 1   | 70 : 30                       | 14.2709      | 13.67                             | 0.03112                              |
| 2   | 60 : 40                       | 19.1320      | 13.97                             | 0.03991                              |
| 3   | 50 : 50                       | 15.9580      | 15.70                             | 0.01999                              |
| 4   | 40 : 60                       | 7.9469       | 20.67                             | 0.02409                              |
| 5   | 30 : 70                       | 6.7174       | 18.83                             | 0.05470                              |

It is shown from Table 2 that the increase of zirconia addition in the composite effect to decreases the porosity, and increases the hardness of β-TCP/ZrO₂. The increase of the hardness of the composite may originate from zirconia which has a higher hardness. The porosity of the samples exhibits values lower than 20% which is in the range of ceramics tolerance of 10 % to 40 % [24]. The high porosity occurs as a result of its different grain sizes; this is due to of processing at high sintering temperatures. With the addition of ZrO₂ filler may suppress the pore growth and in turn to increase the hardness. Both the porosity and the hardness properties are associated with biomedical applications such as bone and tooth implants, and orthopedic [25, 26].

The highest electrical conductivity reached up to 0.05470 S·cm⁻¹ obtained from the sample with a composition of 30:70. The optimum composition of 30:70 with highest electrical conductivity is associated with the lowest porosity of 6.7174 %. We can infer that the decrease in ceramic pores causes an increase of its electrical conductivity.

Figure 3 SEM images of β-TCP:ZrO₂ composites with composition of (a) 70:30, (b) 60:40, (c) 50:50, (d) 40:60, and (e) 30:70 wt%
The SEM images show that all β-TCP/ZrO₂ composites exhibit agglomerations. The sample with the ratio of β-TCP:ZrO₂ composition of 40:60 wt% shows more homogeneous surface morphology compared to other samples. It implies that the sample with 40:60 wt% shows the highest hardness as presented in Table 2. Meanwhile, the sample with the composition of 70:30 wt% for β-TCP/ZrO₂ ratio has the lowest homogeneity resulting the lowest hardness. The surface morphology is closely related to the mechanical properties of the material. Meanwhile, zirconia would be a suitable additive material because of the stable with high biocompatibility and good mechanical properties [27].

The sample achieved the lowest electrical conductivity of 0.01999 S·cm⁻¹ with the composition of 50:50. According to the SEM analyses as in Figure 3, the sample with a ratio of 50:50 is less homogeneous than others.

4. Conclusions
We conclude that the β-TCP/ZrO₂ composites were successfully synthesized using solid-state reaction method. The addition of ZrO₂ affects to enhance the hardness and electrical conductivity of the β-TCP/ZrO₂ composites. The highest hardness of the β-TCP/ZrO₂ composites was obtained for a composition of 40:60. The optimum electrical conductivity was found in the ratio of 30:70 wt%. Furthermore, the porosity was in the range of 7 % to 19 % providing a potential application for regeneration of bone tissue.

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