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Development of Hydroxyapatite-Based Bioceramic Hardness Model Based on Variations in Synthesis Conditions

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Abstract
Hydroxyapatite is a bioceramic which has an excellent biocompatible property and has been widely used in bone scaffolds. However, there has not been any mathematical model that elaborates on the relation between the parameter of synthesis conditions and the mechanical properties of hydroxyapatite. That is why, this article tries to present the relationship model between the hardness of hydroxyapatite based on a variety of synthesis conditions such as sintering temperature, relative density, and the size of the particle. Developing the hardness model is performed based on its relation with the responses from each experimental factor. To validate the model, we compare it with the experimental data, and it indicates that the proposed model has good accuracy.

Keywords: bioceramic, biomaterial, hydroxyapatite, mathematical model

1. Introduction

Innovating bone scaffolds in the field of biomaterial or bone tissue engineering has widely practised. It is because bone scaffolds are to be an alternative solution in bone therapy to compare with the conventional method as in autograft and allograft, which often time undergo scarcity of donor and prone to sickness complication [1].

A prerequisite condition to fulfil an innovation in bone scaffolds is that their property must be biocompatible. One of the materials that have been widely studied in bone scaffolds innovation is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) [2]. Hydroxyapatite is bioceramics which have excellent biocompatible property since they are much similar to human bones. Typically, human bones contain 22% of protein, 8% of water, and the rest 70% of hydroxyapatite [3]. Besides, hydroxyapatite has biodegradable property. Thus, the process of bone therapy can work better [4].

Aside from innovation in hydroxyapatite-based bone scaffolds, any researches related to hydroxyapatite materials also focuses on the efforts to synthesis a hydroxyapatite with superior mechanical properties [5]. Those researches are great importance to develop since hydroxyapatite has poor mechanical property. Hydroxyapatite is brittle [6, 7]. That is why it is worry some when applied on bone since it may not be capable for holding the weight during the process of therapy. Some efforts to improve the mechanical properties of hydroxyapatite that have been done include variations in the parameters of synthesis such as temperature, density, and grain size [8]..

Many experiments related to hydroxyapatite materials innovation have been carried out, yet it is still complicated, hitherto, to get the information on mechanical property model, especially related to the hardness of hydroxyapatite. The very fact is that the

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mathematical model is capable of giving a clear explanation between synthesizing variables and hardness. Hence, if the model can be constructed, it is much likely that the experiment on hydroxyapatite synthesis will work better and focused. Therefore, this article proposes a mathematical model on the hardness of hydroxyapatite based on a variety of synthesis conditions that are frequently performed. The ynthesis conditions which are analyzed here sintering temperature, relative density, and the size of their particles.

2. Hydroxyapatite Hardness Model

Synthesis parameters that significantly affect the hardness of hydroxyapatite are sintering temperature, relative density, and the size of hydroxyapatite particles. [9, 10]. Basically, before reaching a critical point, sintering temperature increases the hardness of hydroxyapatite. This increase goes through the process of solidification or consolidation among particles of hydroxyapatite so that it becomes more solid than the before sintering. However, the heating of higher temperature than critical temperature will cause the particles of hydroxyapatite bigger and complies with the Hall-Petch equation; it will decrease the mechanical property. Besides, over-heating can also decompose the elements of hydroxyapatite, and it can change the phase or compounds of hydroxyapatite. The qualitative relation between relative density and the hardness of hydroxyapatite can be seen from the characteristics of material density. When the density of hydroxyapatite increase, it will make a material stronger in holding the compressive force working on it. While for the size of particles, though Hall-Petch equation states that the hardness of a material is inversely proportional to the size of a particle, but its growth in a material is also related to the increase of its density. Prior to saturation condition, the value of relative density of a material will increase as does the growth of particles. This mechanism will trigger the hardness due to increased material the density. However, after the saturation condition, when relative density is very slow to change while the particles of hydroxyapatite keep growing significantly, then the value of hardness will decrease [11].

The preparation of mathematical models in this article will refer to the models that connect the responses of each experimental factor, as follows [12]:

$$\begin{aligned} Y &= a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1^2 + a_5X_2^2 \\ &\quad + a_6X_3^2 + a_7X_1X_2 + a_8X_1X_3 + a_9X_2X_3 \end{aligned} \tag{1}$$

Where Y represents the response, X_i represents the independent variable, a_i represents an empirical coefficient whose value is determined based on the experimental data and the subscript i indicates factor i. Hence, according to the mechanism that has been described, the hydroxyapatite hardness model can be written as,

$$\begin{aligned} H &= a_0 + a_1T + a_2D + a_3G + a_4T^2 \\ &\quad + a_5D^2 + a_6G^2 + a_7TD + a_8TG + a_9DG \end{aligned} \tag{2}$$

Where H represents hydroxyapatite hardness (GPa), T represents sintering temperature (°C), D represents relative density, and G represents the size of particle (μm).

3. Model Validation on Experiment

This part will explain the comparison between the proposed model, which is the equation above (2) and the experimental data. The validation process was performed through regression analysis using the least square method to obtain information related to the value of empirical coefficients on equation (2). The level of suitability between the proposed model and the experimental results is determined by the R^2 parameter.

The experimental data used in model validation is the result of the experiment conducted by others [8-9,13]. Those three experiments performed in different synthesis conditions. Therefore, by using different data, it is expected to obtain a highly accurate model. After regression analysis has been performed on those three data of experiments, an explicit equation of hydroxyapatite hardness model was obtained as follows:

$$\begin{aligned} H &= -42,3563 + 0,596817D - 0,00882629D^2 \\ &\quad -1,7324G - 0,00695838DG - 0,0116767G^2 \\ &\quad +0,0174367T + 0,00122099DT \\ &\quad +0,00200534GT - 0,0000622314T^2 \end{aligned} \tag{3}$$

The value of R^2 from the comparison between the model on equation (3) and the experimental data is R^2=0,997. Based on this R^2 value, the model proposed in this article has a highly accurate value, as shown in Figure 1. Figure 1(a) shows that the model proposed matches those three data of experiments on the relation between temperature and the hardness of hydroxyapatite. Those three results of experiments show that if the temperature happens to be below the critical point, then the relation between temperature and the hardness is proportional.

However, after passing the critical temperature, the relationship between the two variables becomes inversely proportional. The difference of critical point and the value of hardness from those three data of experiments is due to the difference of synthesis parameters other than temperature. However, those three have a similar pattern.

Figure 1(b) indicates that there is a relation between the relative density of hydroxyapatite and its hardness. It shows that before the saturated condition, the relationship between relative density and its hardness is proportional, but it will be inversely proportional after reach saturated condition. The changes of these properties can be understood as the result of the growth of hydroxyapatite particles though the relative density has been saturated.

In addition, Figure 1(c) indicates that the relation between the size of hydroxyapatite particles and its hardness, in which, before the size of particles becoming big enough, then the relation between the size of the particle and its hardness is proportional, but it will be inversely proportional if the size of particles becoming bigger than critical particle size.

This phenomenon happens due to the increase of hardness as a result of hydroxyapatite solidification. Before the size of particle becoming too big, the hardness mechanism as caused by hydroxyapatite solidification which is more dominant, but the result will be in contrast when those becoming the bigger size of particles and the process of solidification have been slowing down.

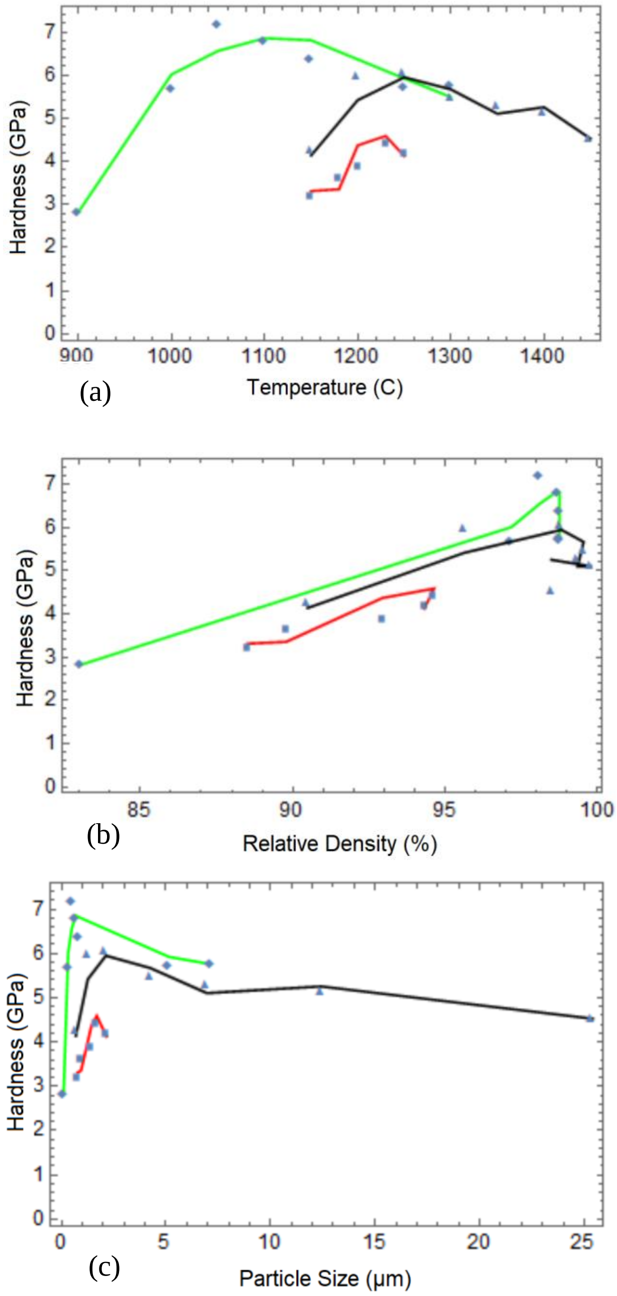
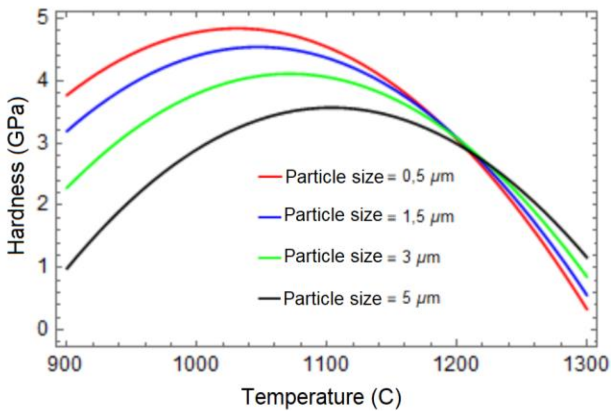
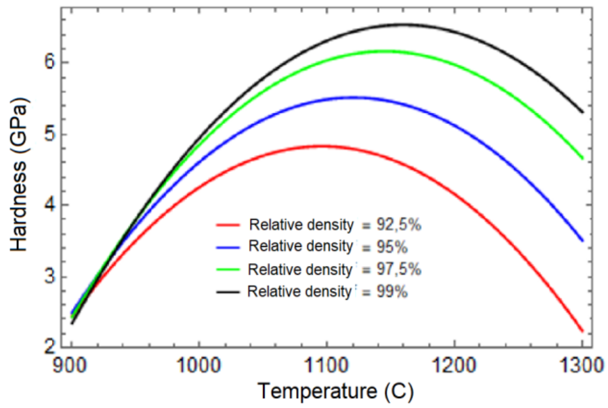


Figure 1. The comparison between the model and experimental result from different bases (i.e., black [8], red [9] and green line [13]) between the hardness and sintering temperature (a), relative density(b), and particle size (c).

To clarify the effect of each synthetic parameter on the changing process of hydroxyapatite hardness, we simulated it, as seen in Figure 2 – 4. Figure 2(a) and 2(b) indicate that the condition of relative density and the size of particle are both constant and similar in their pattern. There is a critical point of temperature that makes the relation between temperature and its hardness changes. Yet, this pattern clearly shows that at the same temperature, the hardness is proportional to the density and inversely proportional to the size of the particle.



(a)

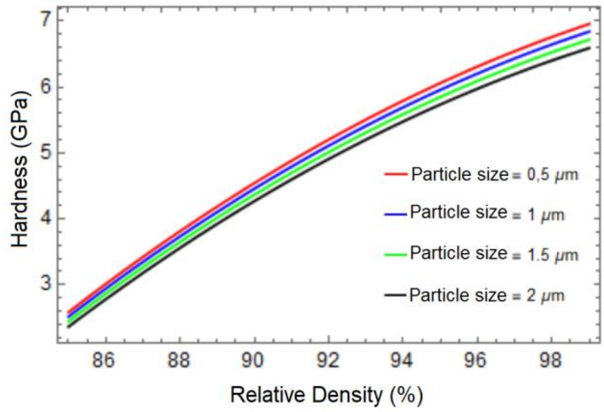


(b)

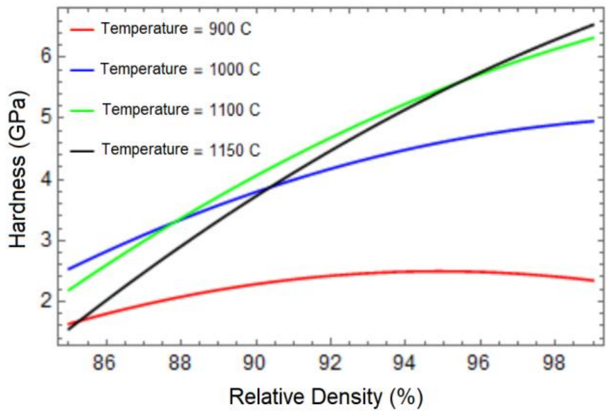
Figure 2. The relation between the hardness and sintering temperature to constant relative density of 90% (a), and to constant size of particle of 3μm (b).

Figure 3(a) and 3(b) indicate the relation between relative density and hydroxyapatite hardness. Through this simulation, it shows that the higher the relative density, the higher the hydroxyapatite hardness is.

This complies with the mechanism already explained on the increasing hardness mechanism due to hydroxyapatite consolidation. At the same value of relative density, the size of the particle and its hardness are inversely proportional, while the sintering temperature has the opposite pattern.



(a)



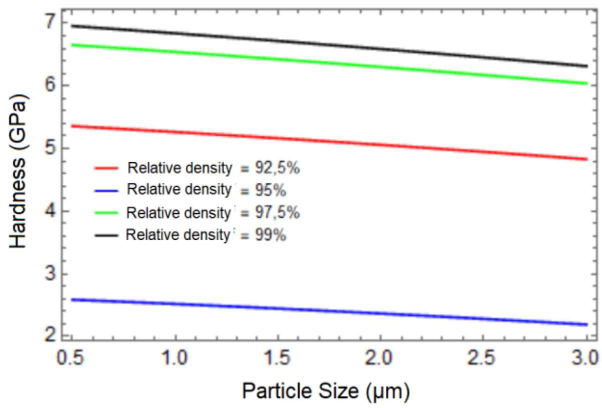
(b)

Figure 3. The relation between the hardness and relative density to constant sintering temperature at 1100℃ (a) and constant particle size of 3μm (b).

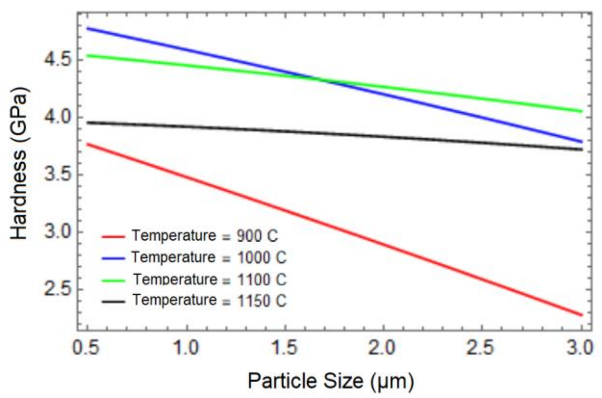
Figure 4(a) and 4(b) indicate the relation between the size of a particle for constant sintering temperature and constant relative density. Both patterns of relation illustrate that the size of the particle is inversely proportional to the hardness and complies with Hall-Petch equation, qualitatively.

For further and more detail observation, the size of the particle on the same condition, there are various patterns. The constant temperature indicates that the relative density of 95% has the lowest value of hardness and relative density of 99% has the highest value of hardness. The constant relative density at the temperature of 900℃ is sintering temperature that is capable of synthesizing hydroxyapatite at the lowest value of hardness.

The temperature of 1000℃ is initially sintering temperature with the highest value of hardness, yet along with the growing size of a particle, the hydroxyapatite hardness at that sintering temperature happens to decrease significantly to compare with sintering temperature.



(a)



(b)

Figure 4. The relation between the hardness and the particle size to constant sintering temperature of 1100 ^{0}C (a) and to constant relative density of 90% (b).

4. Conclusion

This article proposes a mathematical model of the relation between hydroxyapatite hardness and some synthesis parameters. Synthesis parameters observed covers aspects of sintering temperature, relative density, and the size of the hydroxyapatite particle. According to the comparison between the model and the experimental data, a conclusion can be obtained that proposed mathematical model has good accuracy and be capable for giving sufficient explanation on the relation between the hardness of hydroxyapatite and the synthesis parameters. Through the simulation performed in this article, it indicates that in sintering temperature, there is a critical point of temperature that makes the value of hydroxyapatite hardness keeps lowering after reaching this condition. As long as saturated condition has not been achieved, the higher relative density of hydroxyapatite, the higher its value of hardness is. Whereas, the bigger the size of hydroxyapatite particle will decrease the hardness value of hydroxyapatite.

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