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Article

Porous Bioceramics use Albumin as a Pore-Forming Material

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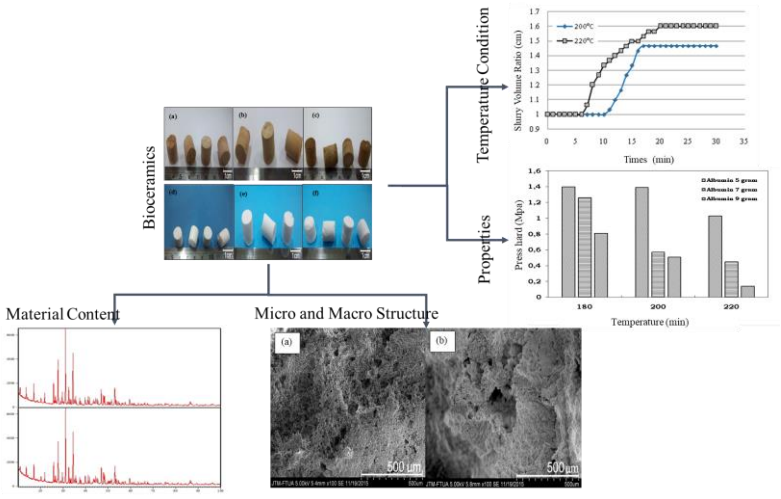
Abstract

Porous bioceramics have been used in biomedical field, especially for bone implant. To generate pores in bioceramics, pore creating substances are added into the process of making ceramic bodies. The purpose of this study is to make porous bioceramics with tri calcium phosphate (TCP) raw material using albumin with variation in the amount of albumin in the raw material and drying temperature on the physical and chemical properties of TCP. Raw material slurry was made by mixing 7 g of TCP, 2 g of starch and 1.5 g of Darvan 821A with 5 g, 7 g and 9 g of albumin in a beaker glass while stirring at a rate of 150 rpm for 3 hours. The slurry was poured into a mold and heated in an oven at 180°C, 200°C and 220°C for 1 hour. Subsequently the sample was burned at 600˚C for 1 hour, following with sintering at 1.100°C for 2 hours. Bioceramic porosity is greater by increasing the amount of albumin and drying temperature, while the compressive strength decreases. Obtained TCP porosity is in the ranges of 68% -78% and compressive strength 0.14-1.4 MPa.

Keywords: *compressive strength, albumin, porosity, tricalcium phosphate*

Graphical Abstract



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Introduction

The number of patients with bone damage continues to increase due to several factors such as traffic accidents, work accidents and osteoporosis. Bone substitute materials used conventionally are derived from healthy bones of other body parts belonging to the patient concerned or other people. Both ways of bone replacement are very prone to causing damage to the part of the bone that is removed [1]. In addition, bone implants can also come from animals or plants. This method has an impact on the possibility of disease transmission carried by animal species and the possibility of being rejected by the human body because of differences. To overcome this problem, biomaterials that can be used as bone implants are needed.

Tricalcium phosphate (TCP) is a synthetic biomaterial that can interact with human body tissues because it has good biocompatibility and can play a role in bone growth and regeneration [2]. Pore characteristics are very important in making bone implants because they affect the rate of bone growth, especially porosity, pore size distribution, morphology, and level of interconnectivity in the implant tissue [3].

Porous ceramics can be classified based on their pore size, namely microporous ceramics, for pore sizes of less than 2 nm, mesoporous ceramics, for pore sizes between 2-50 nm, macroporous ceramics, for pore sizes of more than 50 nm [4]. Researchers have previously reported methods for making pores in ceramics such as the starch consolidation method **(Ramay and Zhang, 2003)**, protein foaming consolidation [5], and direct foaming [6]. Each of these methods has drawbacks both in the manufacturing process and in the results of the products obtained. For example, the process which is quite complicated at the drying stage requires a longer processing time is a drawback of the starch-consolidation method. While the weaknesses found in the protein foaming consolidation and direct foaming methods are weak pore interconnections and non-uniform pore sizes in the resulting porous ceramics [7].

Several pore-forming materials have also been used in the manufacture of porous ceramics, for example, egg yolk [8] and starch [9]. Albumin can be used as a pore-forming agent because it can expand when heated. This article reports the production of porous ceramics using TCP raw materials using albumin as a pore former. Albumin has a greater ability to expand than egg yolk [10]. Effect of variations in the ratio of albumin in the slurry and drying temperature on the physical and chemical properties of the resulting porous ceramics.

Experimental Section

Materials

The materials used in the study were tricalcium phosphate (Sigma Aldrich, Germany), albumin from chicken eggs available at the local market in Pekanbaru, sago flour (UD. Puri Pangan Sejahtera, Indonesia) and Darvan 821 A (R.T. Vanderbilt, USA).

Instrumentation

The tools used in this study included a furnace (Nabertherm, Germany), oven (Cosmos, Indonesia), magnetic stirrer (Dragonlab, China), stainless steel mold, beaker, calipers and ruler.

Analysis of the chemical structure and crystallinity in the porous ceramics prepared was carried out using X-Ray Diffraction (Panalytical, Xpert Pro, Netherland). The pore and surface morphology of the sample was analyzed using Scanning Electron Microscopy (Hitachi, S-3400N, Japan). To measure the compressive strength, the Universal Testing Machine (Tokyo Testing Machine, Japan) was used. The percentage of shrinkage is done by measuring the sample volume before and after the sintering process. Slurry foaming capacity is measured from the change in slurry volume during the heating process.

Density is obtained by weighing and calculating the volume of the sample. The formula for calculating relative density can be seen in equation 1, where the theoretical density of tricalcium phosphate is 3.14 g/cm^3 [11].

Sample porosity is calculated using Equation 2.

Relative density, $\rho_r = \frac{\rho_s}{\rho_t}$ 100% ----------(1)

Porosity = 100% – ρ_r ----------(2)

Where ρs is the sample density, ρr is the relative density and ρt is the theoretical tricalcium phosphate density.

Procedure

This research was started by making a slurry by mixing 7 g of TCP powder and 2 g of starch with 1.5 g of Darvan 821 A and 5, 7 and 9 g of albumin in a beaker glass. Then the slurry was stirred using a magnetic stirrer at 150 rpm for 3 hours at room temperature. The slurry was put into a mold and heated in an oven with a temperature variation of 180°C, 200°C and 220°C for 1 hour. The dried slurry was removed from the mold and continued with the burning stage in the furnace at 600°C with a temperature rise rate of 10°C/minute and a residence time of 1 hour. After that it was continued with the sintering stage at 1,100°C with a temperature rise rate of 2°C/minute and a residence time of 2 hours.

Results and Discussions

The resulting porous ceramics

A mixed slurry consisting of white TCP, starch, Darvan, and albumin is poured into a cylindrical mold. After the drying process at 180°C to 220°C, the slurry becomes more viscous with a brown color. The hardened slurry is removed from a cylindrical mold called a ceramic body. The brown color on the ceramic body increases to dark brown when the drying temperature is increased, as shown in Figure 1a-c.

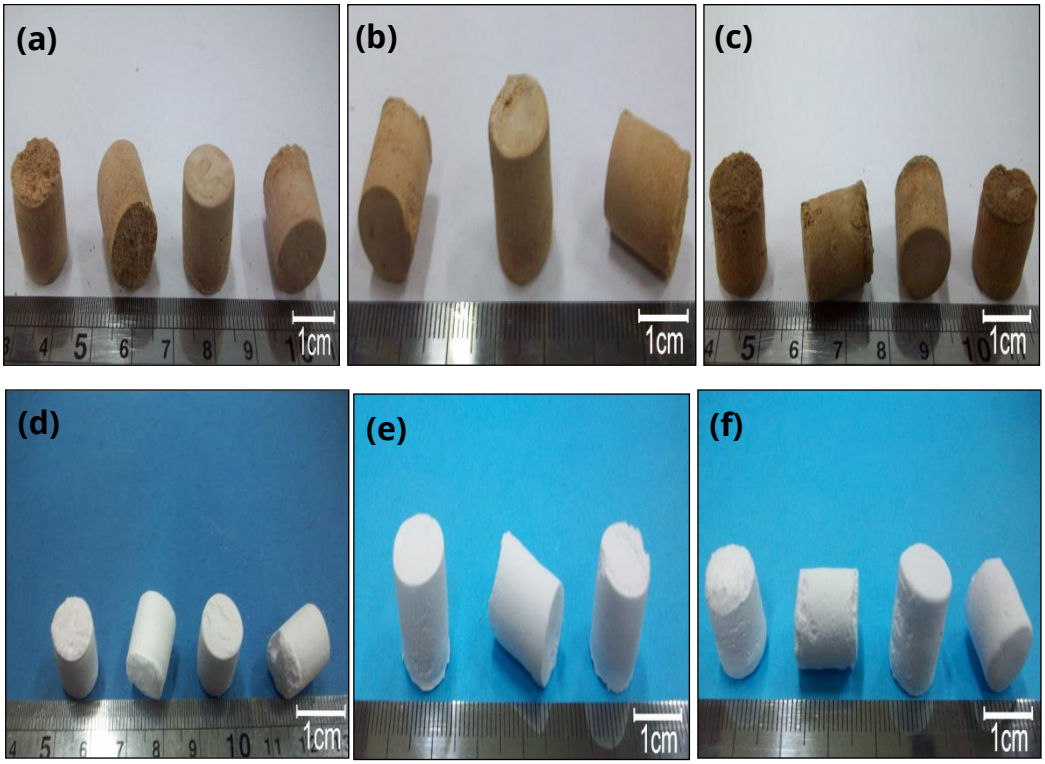

Figure 1. (a) Ceramic body at drying temperature 180°C (b) 200°C (c) 220°C with 5 g of albumin (d) porous ceramic body at drying temperature 180°C (e) 200°C (f) 220°C with 5 g of albumin.

The color change also occurs on the ceramic body during the sintering process from brown to white as shown in Figure 1d-f. This is due to the burning process occurring at a temperature of 600°C. During the burning process, albumin, starch and Darvan 821 A are burned in the ceramic body. The organic materials burn into carbon dioxide which is released into the air while the places left by the organic matter will form pores in the ceramic body. After the combustion process, it is followed by a sintering process which aims to strengthen the bond between the TCP particles on the TCP body wall thereby increasing the mechanical strength.

To determine the effect of the slurry composition on porous ceramics, variations were made on the amount of albumin used, 5 g, 7 g, and 9 g at a sintering temperature of 1,100°C. As the amount of albumin used increases, the shrinkage increases. Shrinkage in ceramic volume occurs due to the loss of mass of organic matter in ceramic materials such as albumin, flour, and Darvan. So the more albumin used will increase shrinkage. In addition, there is a change in shape when the amount of albumin is enlarged and the drying temperature is increased. The ceramic body also experiences increasing shrinkage when the drying temperature increases.

The stages of the slurry development process can be studied by measuring the volume change ratio of the slurry during the drying process. The results of measuring the ratio of slurry volume to the amount of albumin 7 g at 200°C and 220°C can be seen in Figure 2.

During the drying process there are three stages of the process, pre-heating, foaming, and stabilizing. During the pre-heating stage there was a change in protein structure due to heating without the volume change that occurred at the beginning of drying, namely 11 minutes for 200°C and 6 minutes for 220°C. Then the foaming process occurs with an increase in the slurry volume until it reaches the maximum volume. This stage occurs in 12-17 min for a drying temperature of 200°C, while for a drying temperature of 220°C the foaming stage occurs in 7-20 minutes. This expansion occurs due to protein denaturation and encourages the formation of foam due to increased heat [12]. Increased drying temperature causes faster foam formation. This is due to the faster denaturation of proteins. At 18-30 minutes there was no change in volume for a drying temperature of 200°C, whereas for a drying temperature of 220°C there was no change in volume at 21-30 minutes or it had reached the stabilizing stage.

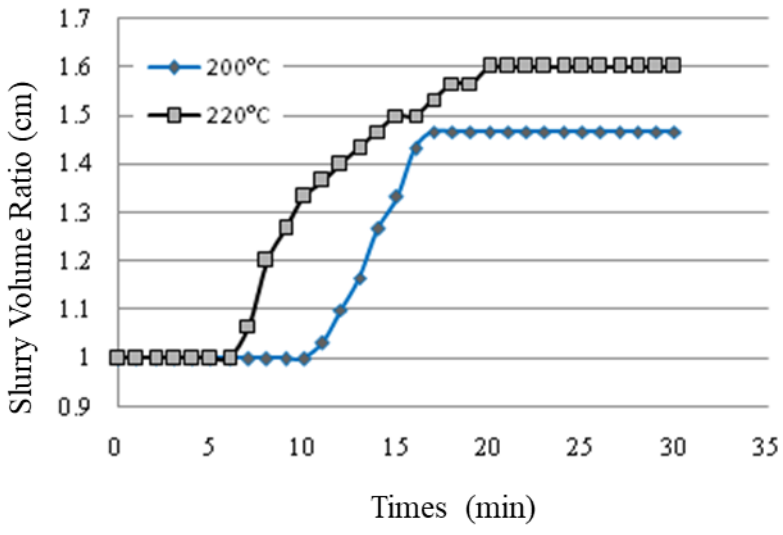

Figure 2. Slurry volume ratio during the drying process at 200°C and 220°C.

At low drying temperatures, the slurry expansion capacity is lower. This is caused by the reduced ability to expand albumin when the temperature is lowered. This will cause the number of pores formed and porosity to decrease [13] and the regular arrangement of atoms [14]. This is in accordance with the results of the microstructural analysis of the samples with drying temperatures of 200°C and 220°C in Figure 7.

Effect of drying temperature and amount of albumin on the physical characteristics of porous ceramics

The physical characteristics of the ceramics measured in this study were the percentage of shrinkage, porosity and density. After the sintering process at a temperature of 1100°C the ceramic samples experienced a decrease in body volume (shrinkage). Figure 3 shows that the increasing the amount of albumin, the higher the shrinkage percentage. The volume shrinkage that occurred for samples with 5 g albumin composition was 32.11% - 33.77%, for samples with 7 g albumin composition experienced a shrinkage percentage of 35.48% - 36.27%, and for samples with 9 g albumin composition experienced a shrinkage percentage of 37.47% - 38.17%. The sintering temperature has a direct impact on the final ceramic structure [15].

The initially dispersed TCP particles will contact each other and form clusters during the burning and sintering processes. Burning albumin will leave pores on the ceramic wall. The pore will be the space which moves from the center towards the outer surface of the body during the sintering process and at the same time the particles move to the inner surface of the ceramic body. The movement of the particles causes shrinkage of the body [16]. So that the more amount of albumin used, the higher the shrinkage percentage. The shrinkage of the ceramic body is also affected by the drying temperature. The higher the drying temperature, the higher the shrinkage percentage.

In addition, the higher the drying temperature causes the porosity to increase. At high drying temperatures, the expansion capacity increases and the pores formed also increase. Figure 4 shows the porous TCP porosity in the range of 67.7%-72.77% for 5 g of albumin, 70.09%-75.35% for 7 g of albumin, and 70.36%-78.13% for 9 g of albumin.

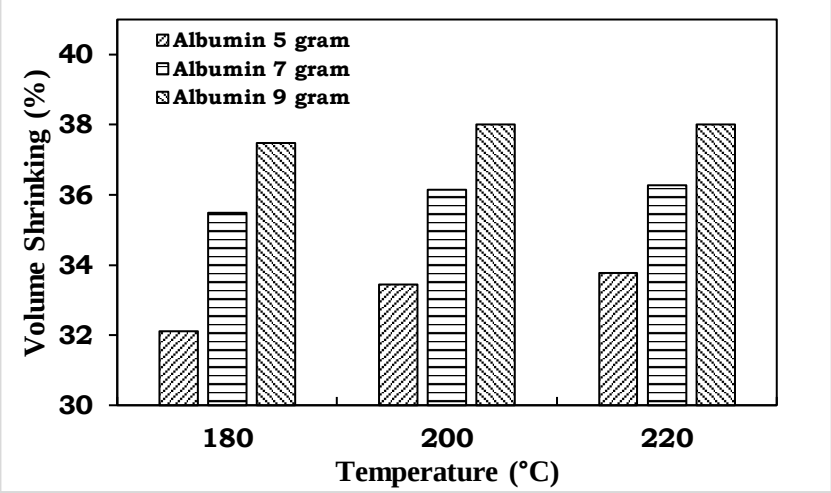

Figure 3. Graph of the relationship between the percentage of shrinkage and drying temperature of 180°C, 200°C, 220°C with albumin composition of 5 g, 7 g and 9 g.

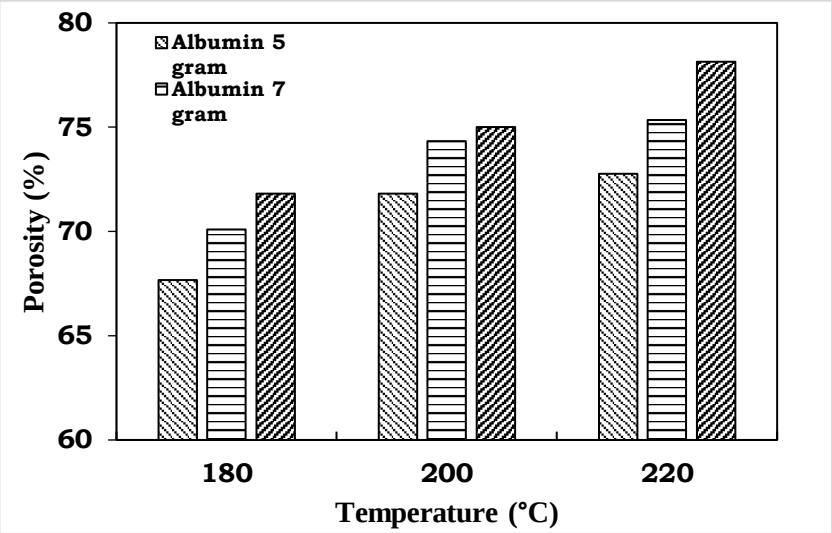

Figure 4. Graph of porosity relationship to drying temperature 180°C, 200°C, 220°C with albumin composition of 5 g, 7 g and 9 g.

Effect of drying temperature and amount of albumin on compressive strength

Compressive strength is a very important factor in determining the feasibility of porous ceramics as bone implants. From Figure 5 it shows that the more the amount of albumin used, the compressive strength will decrease. This is due to an increase in foaming capacity when the amount of albumin increases in the slurry. High foaming capacity will result in large pore sizes and increased porosity.

Gibson & Asby (1988) stated that the compressive strength of porous ceramics will decrease with increasing porosity [17]. And the higher the drying temperature, the more compressive strength will decrease. The resulting compressive strength of porous TCP is in the range of 1.03-1.4 MPa for 5 g of albumin, 0.45-1.26 MPa for 7 g of albumin, and 0.14-0.81 MPa for 9 g of albumin. There are slices of several compressive strength values caused by different drying temperatures and struts thickness.

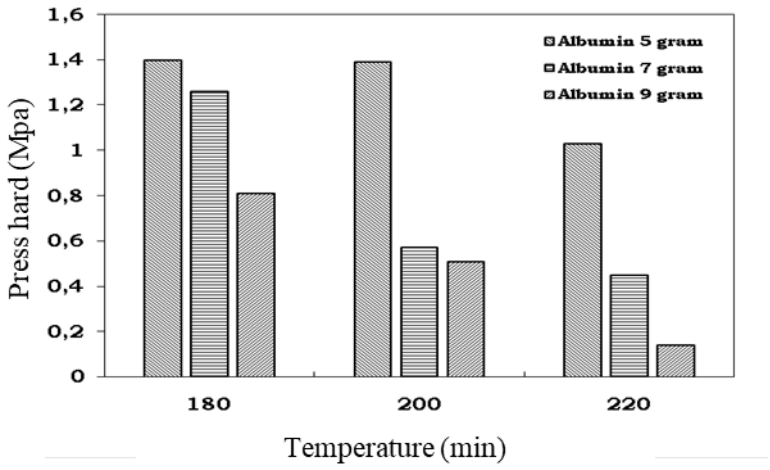

Figure 5. Graph of the relationship of compressive strength to drying temperature 180ºC, 200ºC, 220ºC with albumin composition of 5 g, 7 g and 9 g.

Effect of drying temperature and ratio of albumin composition on macro and microstructure

The difference in drying temperature affects the structure of the porous ceramics [12] stated that as the drying temperature increases, the pore size also increases. This is because drying at low temperatures will reduce the foaming capacity. In Figure 6a it has a pore size of 50-150 µm smaller than in Figure 6b it has a pore size of 200-350 µm.

The microstructure of porous ceramics will also change due to an increase in drying temperature. In Figure 7b it can be seen that the pore distribution is more even and the pore size is larger when compared to 7a. At higher drying temperatures, the pores spread to the pore walls which are less dense and thinner [18]. The smaller the pore size causes the ceramic to become denser, so that the compressive strength of the ceramic will increase as shown in Figure 7.

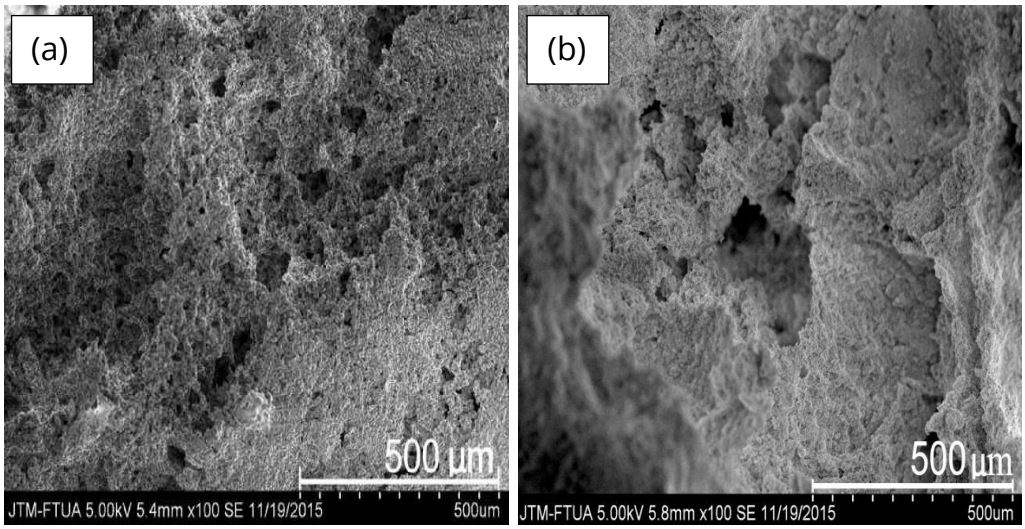

Figure 6. Sample macrostructure with drying temperature (a) 200°C (b) 220°C with 9 g of albumin.

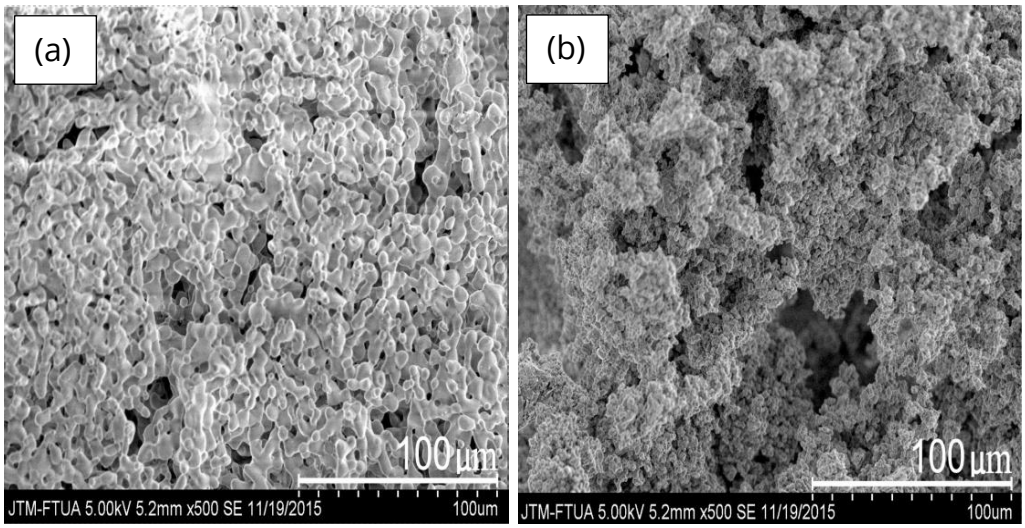

Figure 7. Sample Microstructure with Drying Temperature (a) 200°C (b) 220°C with Total Albumin 9 g.

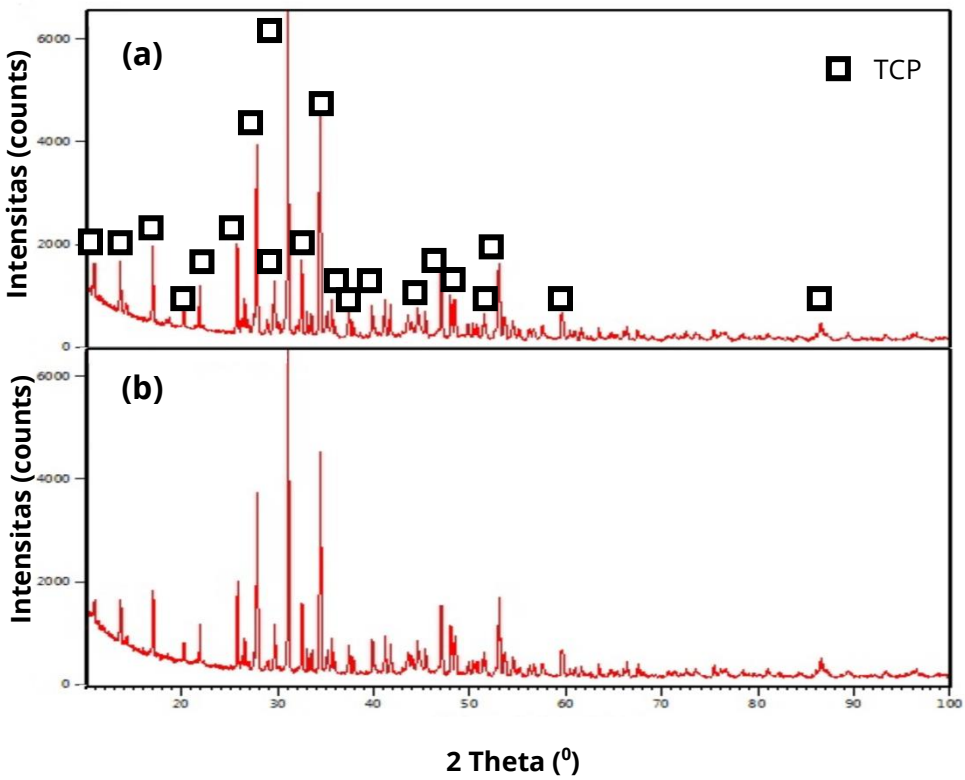

Figure 8. Graph of Effect of Albumin Addition on Chemical Structure (a) TCP Powder, (b) 5 g of Albumin Addition.

The XRD analysis aims to determine the effect of adding albumin on the material content of ceramics which have become porous ceramics with raw ceramic powder. Figure 8 shows a comparison of the content between TCP used as a raw material and TCP that has been made into porous ceramics.

The crystal analysis pattern of the porous ceramic is the same as the crystal pattern of the raw material ceramic powder or in other words the addition of albumin and the sintering process at 1,100°C does not affect the chemical composition of the ceramic material. In other words, the sintering process is only to remove organic compounds without changing the crystal content in the ceramic. Sintering generally plays a role in stabilizing the metal and detoxifying the metal, and without melting the material and changing the metal components [19].

Conclusions

Porous TCP has been successfully prepared by the protein foaming-starch consolidation method using albumin as a pore former. The albumin composition and drying temperature affected the physical properties and did not affect the chemical properties of the porous TCP. The greater the amount of albumin and the higher the drying temperature, the greater the percentage of shrinkage, the greater the porosity, the smaller the density, and the smaller the compressive strength. The obtained TCP has a porosity of 67.7–70.36% for 5 g of albumin, 71.8-75% for 7 g of albumin, and 72.8-78.1% for 9 g of albumin. The resulting compressive strength is 1.03–1.40 MPa for 5 g of albumin, 0.45–1.26 MPa for 7 g of albumin, and 0.15-0.81 MPa for 9 g of albumin.

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