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Effect of Calcination Temperature on Microstructure, Porosity and Hardness of Cao/Sio2 Nanocomposites for Bone Implants

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ABSTRACT

This research is a study on the effect of calcination temperature on microstructure, porosity, and hardness of CaO/SiO2 nanocomposites for bone implants made from natural materials of pensi shells and silica sand. The purpose of this study was to determine the effect of variations in calcination temperature on the morphological analysis of structural form, porosity, and hardness of CaO/SiO2 nanocomposites in samples for biomaterials and to determine whether CaO/SiO2 nanocomposites derived from pensi shells and quartz sand are possible to be applied as biomaterials. The results showed that the effect of variations in calcination temperature on the microstructure of bone implant samples was that the higher the calcination temperature would affect the microstructure's shape on the surface of the model where the surface formed was widening, and the grain size was getting smaller. In the porosity, it can be seen that there is diffusion between one grain and another. The grains melt with each other and close the pores from the outside, resulting in compaction at a temperature of 1000°C with a porosity value of 0.005% and the best hardness value of 4.8 kg/mm2.

Keywords : *Biomaterials, Nanocomposites, Bone Implants*

I. INTRODUCTION

Biomaterials have several broad meanings, especially in materials science and medical science. According to Widya [1] biomaterials in medical science are biological systems that can interact with implant materials. Meanwhile, in material science, biomaterials are natural materials or synthetically engineered materials that can interact with biological systems and are connected to medical devices. One of them is the application of biomaterials in manufacturing bone implants. According to the Minister of Research, Technology, and Higher Education 2017, Muh Nasir, the need for bone implants in Indonesia is very high, reaching 80,000-100,000 pieces per year. This happens because of the high number of accidents that result in fractures to osteoporosis in the bones [2]. Based on these data, it was found that from 2014 to 2019, the number of traffic accidents was higher, which reached 107,500 cases, and 79.8% of traffic accident victims experienced fractures which resulted in the need for bone implants (osteosynthesis) to increase.

Thus, in recent years the demand for biomaterial applications has increased. For example, based on metric info data in 2009, the world's application of biomaterials in 2008 reached a total of US$ 212.8. Furthermore, biomaterials predicted to be used as groin replacement implants will increase to 272,000 by 2030. The same thing also happens in Indonesia, where there are many cases of bone damage or trauma triggered by unhealthy diets, natural disasters, congenital disabilities, infections, and points of traffic accidents. However, the increasing demand for bone implants is not accompanied by a balanced production of local implants, so imported bone implants still dominate the Indonesian market. This is due to the high cost of bone implants, which reaches around

US$ 400, making it difficult for people to get them [2]. Therefore, bone implant biomaterials are needed on an ongoing basis in sufficient quantities and are also readily available and at an economical price [3].

Based on the problems above, further research is needed on the innovation of bone implant synthesis. In a previous study, Lukman [4] used CaO from limestone containing 82.5% and SiO2 from quartz sand with a range of 97.5%. This bone implant has a hardness value of 64.03% at temperatures of 500ºC, 600ºC, 700ºC, and 800ºC. The results showed that at a temperature of 500-800ºC, a CaO/SiO2 with dicalcium silicate impurity phase2. The increase in temperature causes the porosity and the hardness to decrease. It can be seen in the microstructure that the grain size is getting bigger, and the pores are getting more and more. The porosity decreased, and the hardness value increased [5].

The second study of Kurniawan et al. Kurniawan [3] explained using shellfish waste and Sidoardjo mud to synthesize CaO and SiO2 with the calcination process and their characterization using the Vickers hardness and SEM, BET. The results of hardness characterization were 109.1 ± 5.22 VHN at a heating temperature of 900ºC. Then for the effects of morphological characterization, at this temperature, lumps formed and enlarged granules with smaller pore sizes [6]. As for the porosity analysis at this temperature, the surface area value is 23,843 m2/g, and the pore volume is 0.007 cc/g. From the research, it can be concluded that increasing the heating temperature causes the hardness to increase and affects the shape of the microstructure and surface area on the surface of the sample.

Furthermore, other additives that can be used in the manufacture of this CaO/SiO2 nanocomposite are pensi shells (Corbicula moltkiana). According to Nadiah [7], pensi shells are waste thrown away by the community and will be very easy to find in West Sumatra, especially in the Maninjau Lake area, where there is still a lot of waste pensi shells that need to be appropriately treated. Pensi shells have a potential source of calcium (Ca) with a Ca content of 26-30% in raw form. The pensi clam shell can be used as a source of CaO content because pensi clam shell contains more than 90% CaO. In addition to pensi shell waste, one of Indonesia's natural potential in mining minerals is quartz sand with dominant quartz (SiO2) with a purity of up to 95-97%.

Seeing the high content of CaO from pensi shells and SiO2in quartz sand, this study tried to apply it as a bone implant biomaterial. Based on the facts in the field, there is no good treatment for using pensi shells waste. According to research [8], the synthesis of CaO/SiO2 in the wollastonite phase, dicalcium silicate, and diopside are very well used as bone substitutes or artificial bones.SiO2 impurity phase was found at a temperature of 800oCand. That temperature decreased porosity, and the pore surface was agglomerated and enlarged in the nanocomposite sample.

II. METHOD

This research is experimental research with a quantitative research approach. Empirical research is one type of research to determine the effect of a variable on other variables. The analysis of the results of this study will describe the relationship between the effect of temperature variations on the calcination process of pensi shells and quartz sand with the results of hardness and porosity morphology tests.

At this stage of making samples, the processing of materials that will be used in making samples is carried out for testing the hardness, porosity, and morphology of the surface microstructure of the model. Pensi Shell Processing, the material of this research includes several stages.

The first step is to prepare pensi shell waste. Wash the pensi shell thoroughly with running water. Then do the pensi shell drying for one day. Soaking the pensi shells in HCl for 1 hour, then washing with distilled water and drying at room temperature for 24 hours. Place the pensi shell in the oven at 105°C for 30 minutes [9]. The surface of the pensi is ground roughly with a mortar and pestle to be calcined in the furnace. Place the clam shells in a steaming bowl and cover them with aluminum foil. The pensi shells were calcined for 6 hours at 900ºC. After that, cool for 12 hours and remove from the furnace. Next, grind the calcined pensi shell to get a white powder. Furthermore, the results in the white powder were sieved using a 200 mesh (0.74 m) sieve and then tested for CaO powder using XRD.

The next stage is the processing of silica sand. The sand was milled using HEM for 5 hours. Furthermore, the crushed silica sand was sieved using a 200 mesh sieve, and the sand that passed the sieve was soaked in 2M HCl for 12 hours. Then the sand is washed with distilled water until it is not yellowish and dried in an oven at 80°C. The dry sand is reacted with NaOH at 95°C. The solution was stirred at 300 rpm for 3 hours. They were then filtered using fine filter paper by adding 20 ml of boiling distilled water. The solution that passed the filter was then stirred at 100 rpm, and HCl was added to form a gel. The gel was left for 18 hours, then washed five times with distilled water and dried at 80°C. Then it is ground to obtain powdered silica and tested using XRD. Next, make a CaO/SiO2 composite. Weigh 52% CaO powder and 48% SiO2 powder. Then dissolve it with 100 ml of

methanol. Then the solution was stirred at 300 rpm for 90 minutes. Then the mixed solution was calcined with a temperature variation of 700-1000°C for 3 hours using a furnace. Then grind it back to powder.

Cao/SiO2 powder was dripped with 5 ml of PVA solution to prepare bone implant samples. Then print the model using the mold and wait for it to dry. After that, the sample testing stage was carried out. The first step is X-ray diffraction testing. Before testing the hardness and microstructure, the composite powder was first characterized using XRD to see the peaks of the crystals formed. The test step is that the sample is placed on an aluminum plate, then the plate is inserted into the XRD tool. After that, set the angle to 2ɵ on the High Score Plus computer software connected to the XRD tool, then wait for the component results on the sample formed from the High Score Plus software.

For the hardness test using Vickers microhardness, in this study, a hardness test was carried out based on ASTM E 384. The test method measures the dimensions of the test object, including length, width, and thickness. Then turn on the test tool (microhardness vicker). After that, choose a load of 25 gf. Place the sample in the vise, then find focus by raising the specimen, placing it in the most precise position, and aligning the vertical lines, then press "Reset." Set a dwell time of 5 seconds. Press the start button, and the indenter will push automatically. Observe the pressure trace, then measure the length of the diagonal pressure trace horizontally (d1) by positioning the vertical parallel lines at both corners of the diagonal imprint, press the horizontal position (d1), then press the encoder button. Then rotate the encoder 90° counterclockwise, measure the diagonal length of the horizontal pressure trace (d2), press the encoder button again, and read the hardness test results.

In electron microscopy examination, for testing the surface morphology of bone implant samples, samples that had been calcined with temperature variations were printed with a size of 3 mm x 3 mm x 5 mm and then sent to P3GL Bandung for characterization by SEM.

Then do the porosity test. The test is carried out using the finished sample being weighed first for its dry mass. Then soaked in water for 1 hour and weighed the wet weight. After entering the data from the dry weight and wet weight of the sample in the equation (1).

$$P = \frac{Mb-Mk}{Vb} x\ \rho_{air}\ x\ 100\%. \quad (1)$$

III. RESULTS AND DISCUSSION

It can see the data from the characterization of pensi shells using XRD is in Figure 1. X-ray diffraction aims to determine the lattice parameters and identify the structure, grain size, and crystal elements. In this study, XRD is used to see the pattern of the resulting peaks.

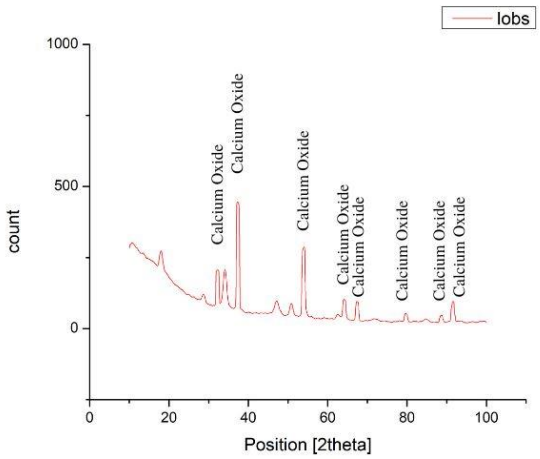

Fig. 1. Results of characterization of shells into CaO

The results of pensi shell extraction using the calcination method obtained a CaO phase of 92%. Furthermore, the XRD results of silica sand can be seen in Figure 2.

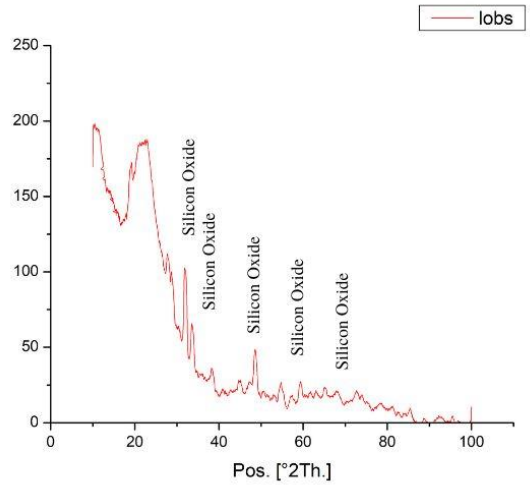

Fig. 2. Silica sand characterization

For the extraction of quartz sand obtained amorphous SiO2. Furthermore, the XRD results of CaO/SiO2 at a comparison of XRD CaO/SiO2 results with temperature variations of 700-1000ºC can be seen in Figure 3.

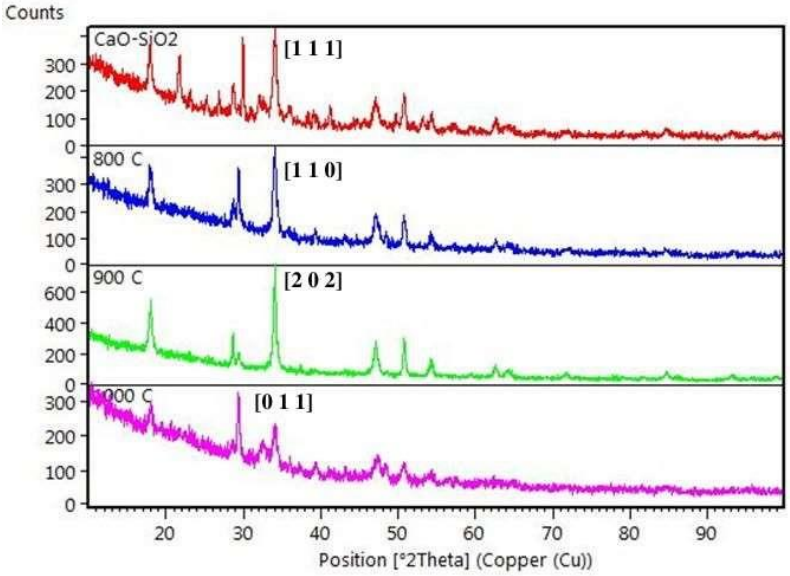

Fig. 3. Comparison of XRD CaO/SiO2 results with temperature variations of 700-1000ºC

Results XRD characterization of CaO/SiO2 composites with temperature variations of 700-1000°C where at a temperature of 1000°C the impurity peak is no longer found, which shows that all element atoms occupy crystal symmetry according to the dicalcium silicate phase and are excellent and potential composite phases. For use as artificial bone material. Data characterization results using SEM can be seen in Figure 4.

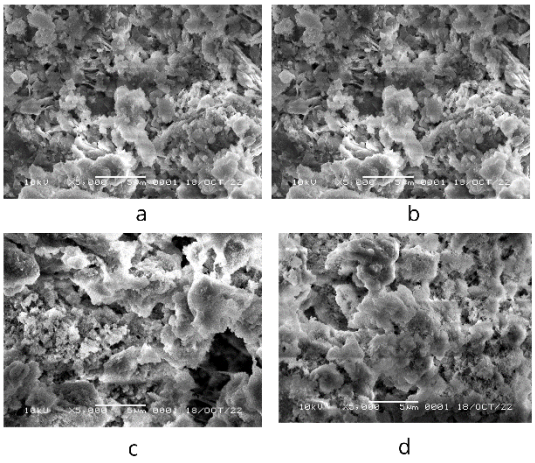

Fig. 4. The result of a Scanning Electron Magnetic (SEM) characterization a) at 700°C, b) 800°C, c) 900°C and d) 1000°C

Bone implant samples were tested at the Metallurgy and Metrology Laboratory, Faculty of Engineering, State University of Padang. Tests were carried out on three surfaces of bone implant samples (3 points). The following data on the results of hardness testing on bone-implant samples obtained can be seen in Table 1.

Table. 1. Hardness test data for bone implant samples

Temperature Variation (°C)	Point	Diagonal Indentor (mm)		Diagonal mean density (mm)	Price Vickers Hardness (kg/mm^2)	Average Vickers Hardness Price(kg/mm2)
		d1	d2			
	1	115,05	115,05	115,05	3,5	
700	2	111,28	105,50	108,39	3,8	3,63
	3	105,21	106,74	105,97	3,6	
	1	116,89	103,77	110,33	3,7	
800	2	101,87	99,28	100,57	4,1	3,86
	3	111,26	111,05	111,15	3,8	
	1	103,28	96,74	100,01	4,5	
900	2	102,76	102,76	102,76	4,4	4,43
	3	102,38	102,38	102,38	4,4	
	1	103,34	98,46	100,9	4,6	
1000	2	98,45	98,43	98,44	4,8	4,73
	3	98,59	100,71	99,65	4,8	

From the table, it can be seen that the higher the calcination temperature, the higher the hardness value. Next is the results of the porosity test of the porosity data. The test is to see the solidification process by applying calcination temperature variations. The test results can be seen in Table 2.

Table. 2. Table of bone implant porosity value

No	Heating Temperature(°C)	Porosity (%)
1	700	0,19
2	800	0,18
3	900	0,007
4	1000	0,005

Testing of mechanical properties on bone-implant samples was carried out to determine how the effect of temperature variations on the hardness of bone implant samples in addition to testing the microstructure and porosity. The temperature variations in the bone implant research samples were 700°C, 800°C, 900°C, and 1000°C. When referring to the materials used in this study, namely CaO/SiO2 from pensi shells and silica sand as an additive to the sample and the mixed material, namely using polyvinyl alcohol in forming bone implant samples. The process of healing bone fractures in the medical world is usually synthesized materials that can be taken from the patient's body (autograft), from the body of another patient who has a close family relationship (allograft), or from animals (xenograft). However, medically these materials can pose several risks, including causing excessive pain due to bone surgery treatment in two different places and often a rejection of the patient's body [10] for this reason, natural polymer materials were used in this study. as a base material for forming bone implant samples.

In the pensi shell calcination process, the aim is to convert a carbon compound into an oxide. The initial content in the pensi shell is CaCO3 after the calcination process, and the content turns into CaO because it releases water, CO2(carbon dioxide), or other chemically bound gases [11]. This CaO content is used to manufacture composites as a calcium source. The optimal temperature for calcination in this study was 900° for 5 hours, referring to research by [7]. At this temperature, the compound bonds in CaCO3 will be broken if heat energy is given (calcination), which refers to the thermal decomposition to produce calcium oxide compounds (CaO) [12]. From the calcination process in this study, the CaO content was 95% and other impurities around 5%, where the higher the purity of CaO, the better the mechanical properties. CaO will reinforce the sample because of its high calcium content. Impurities that are more than 10% will affect the purity of the calcined results obtained. For that, when making samples, it must be considered to get maximum results and small impurities in the model. The CaO content of pensi shells in this study was higher than in previous studies. Namely, in research [6], the calcium content in ale-ale shells was 94%. Thus, the use of pensi shells to be synthesized into CaO is very good for use as a natural base material.

Next is the synthesis process on silica sand, carried out to obtain SiO2 compounds. Silica sand itself has a combined composition of SiO2 and other impurities. Amorphous silica can be extracted or synthesized from silica sand using precipitation, sol-gel, acid removal, and alkaline extraction methods. Where the silica formed will resemble a gel [1]. In this research, the method used in extracting or synthesizing silica sand is the sol-gel method, in which the resulting silica is after characterization using XRD Amorphous.

CaO/SiO2 biomaterials [4] are bioactive. In this study, during combustion or calcination at a temperature of 700°C, the peak for the diffraction pattern formed was wollastonite. When the temperature increased to 800°C, the mountains conformed to the coesite (SiO2) phase. At a temperature of 900°C, the presence of at least an impurity phase coesite. Meanwhile, at a temperature of 1000°C, the impurity peak was no longer found, which indicates that all the element atoms occupy a crystal symmetry that corresponds to the dicalcium silicate phase and is an excellent composite phase and has the potential to be used as artificial bone material.

The microstructural characterization test using SEM was used to see the results of the pore surface on bone-implant samples. At a calcination temperature of 700°C, the pore surface is slightly even, and this uniform pore surface is formed due to interactions between grains. The grains are attached so that the grain boundaries disappear. At a temperature of 800°C, the even surface decreases, and when heated to a temperature of 900°C, the more pores and the larger the granules. Increasing the heating temperature causes the grain size to increase. The increase in grain size that is not accompanied by pore removal and interactions between grains causes coarsening. Meanwhile,

at a temperature of 1000°C, the surface formed is more comprehensive, and the grain size is getting smaller. On heating, with a higher temperature, the pores will be closed entirely, and the grain boundaries will disappear.

Testing of mechanical properties, especially the hardness test, is carried out to see the hardness of a sample when given a significant pressure. Theoretically, an increase in temperature will contribute to an increase in hardness due to interactions between grains. The interaction between grains that reduces the number of surfaces and grain boundaries causes a smaller dislocation field which causes a shift so that the material has a high hardness[13]. Based on the test results from this study, the highest hardness was also found in combustion at a temperature of 1000°C.

In the sintering process, the granules undergo two mechanisms: coarsening and compaction. At a temperature of 700-800°C, the porosity of the material increases. Coarsening tends to be more dominant at this temperature than compaction [14]. The larger granules are not followed by compression, so pores are formed. While heating at 900-1000°C, the percentage of pores decreases. This may occur because the sample has undergone compaction. When the temperature increases to 900°C, a sintering process occurs, and diffusion occurs between the grains with one. The granules melt with each other and close the pores from the outside so that the compaction process appears [15].

IV. CONCLUSION

Based on research that has been done, the effect of variations in calcination temperature on the microstructure of bone implant samples is that the higher the calcination temperature given will affect the shape of the microstructure and the porosity of the sample surface, whereas when the combustion temperature is 1000°C the surface formed is more comprehensive and the grain size is smaller on the portion where the sintering process begins, and there is diffusion between grains with one another. The grains melt with each other and close the pores from the outside, resulting in a compaction process at 1000°C with a porosity value of 0.005% and the best hardness value at 1000°C of 4.8 kg/mm2.

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