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The Influence of Lampung Natural Lime Temperature and Heating Time on The Physical Properties and Hardness of Hydroxy Products (HA)

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ABSTRACT

Hydroxyapatite (HA), a vital component for tissue and porous applications, holds promise in bone regeneration. Derived from calcium carbonate (CaCO3), it's essential for biocompatibility in human bone replacement. This study aims to harness Lampung Province's limestone as a raw material for HA synthesis, simulating human bone properties. Ball milling (2, 3, and 4 hours at 300 rpm) and sintering (600 °C, 800 °C, and 1000 °C for 2, 3, and 4 hours) were varied, with analyses encompassing FTIR, XRD, SEM-EDX, and Vickers hardness.

Mountain branch limestone, comprising 97.43% CaCO3, serves as a suitable bone substitute. FTIR spectra of calcined lime powder exhibit PO43-peaks at 1025.45 cm1, Ca-O vibrations at 1413.59 cm1, and OH groups at 3030.33 cm1, mimicking commercial HA. XRD patterns closely resemble the commercial product, with a peak at 2 32.26°. SEM-EDX analysis at 1000 °C for 4 hours reveals a uniform microstructure. Among milling processes, 2-hour milling at 300 rpm exhibits the highest calcium and phosphate levels in EDX results. Vibration testing indicates peak hardness at 1000 °C and 4 hours of processing.

Keywords: *Lime Stone, Hydroxyapatite, FTIR, XRD, SEM.*

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INTRODUCTION

In broad terms, bones have several functions, including mechanical, protective, metabolic, and hematopoietic functions, or they also function to support the human body and protect other soft tissues, such as the heart, liver, lungs, and others. The bone has an important part, namely the marrow. In the marrow are important minerals such as calcium and phosphate (Sihombing et al., 2012). Serves as a place for the development of red blood cells in the process of bone formation (Mahanani, 2013). Damage to bone tissue can cause structural defects that will cause impaired body function due to the loss of minerals such as calcium and phosphate. The main factors in bone implants are materials that are able to be accepted into human body tissues, firmly unite and function in the body tissues to be implanted, must be biocompatible and toxic, and have bioactive properties such as hydroxyapatite.Fractures are also known as broken bones. Fractures are the breaking of bone or cartilage due to collisions, accidents, disease, or a process of bone degradation resulting in fractures (Asrizal, 2014).

Previous studies have described the production of hydroxyapatite using natural calcium as a source, including the use of waste shells, egg shells, and coral. In addition to limitations on waste shells, egg shells, and coral, the utilization of these marine organisms can hamper environmental issues because coral or coral reefs are habitats for various types of fish. So for that reason, limestone is the choice in the hydroxyapatite process (Prabaningtyas, 2015).Limestone, or limestone, is a type of rock that is still found in almost all of Indonesia. Limestone is a type of rock that contains a lot of calcium carbonate. The type of carbonate mineral found in limestone is aragonite (CaCO3), which contains a lot of minerals and, at a certain time, will turn into calcite (CaCO3) (Noviyanti et al., 2015).The use of limestone as implants used in bones and to repair parts of human bones is done by converting limestone into a type of hydroxyapatite (HA) powder, which first seeks a chemical composition to become CaO (Margareta et al., 2015). Where is the main laden CaO for a powder manufacturing process and must achieve a Ca/P ratio of 1.67 (Putri et al., 2015).

As well as forming the same crystal structure in hydroxyapatite for human and animal bones, the use of this powder must go through several stages, namely, using a ball mill machine to turn limestone into powder. The limestone chunks are washed with clean water after the limestone is cleaned. The limestone is dried and then crushed into powder. After that, it is mixed with sodium hydrogen phosphate (Na2HPO4*2 H2O) with distilled water, then in a ball mill, oven, compaction, and sintering to be analyzed by FTIR, XRD, SEM-EDX, and hardness tests to obtain materials that meet the needs of human bones.Hydroxyapatite (HA) is a chemical element that has the mineral apatite with the formula Ca10(PO4)6(OH)2 (Margareta et al., 2015). At this time, much hydroxyapatite is needed to repair, add to, and reconstruct bone tissue that is already brittle or broken in soft tissue.Until now, bone defects have been a serious problem in orthopedics. When a bone filler is damaged or broken, it is necessary to look for a filler material that is similar to the bone structure; in this case, what is needed is a mineral composition that is bicompatible and bioactive. So hydroxyapatite (HA) limestone can be used in world health as a substitute or filler for damaged bones.

For bone repair, it is necessary to develop materials (micro and nano) that are compatible with limestone. A research material from nature that can be effective in consolidating human bones with limestone in the hydroxyapatite (HA) process, which has recently been proposed for biomedical development.In previous studies, using the parameters of mixing CaHPO4, 2H2O, and CaCO3, and then adding distilled water, with a grinding time of 15, 30, 45, 60, and 180 minutes and a rotational speed of 200, 400, and 600 rpm, the mixture was heated to a temperature of 80 oC for 24 hours.This research will use material from mountain limestone, which is converted into micropowder. Which will be used as a substitute for calcium and phosphate for bone with a milling speed of 300 rpm for 2, 3, and 4 hours and sintering temperatures of 600^{o}C, 800^{o}C, and 1000^{o}C.

METHODS

It is made by taking limestone chunks, then washing them using distilled water and then drying them, then crushing the limestone chunks using a hammer (hammer) and then grinding them into powder, then sifting them (mess). After that, the powder was mixed using sodium hydrogen phosphate and distilled water, then in a ball mill, then in the oven, then sintered and compacted, and then observations were carried out using FTIR, XRD, and hardness testing was carried out at BPPT Serpong, SEM, and EDX at the University of Lampung. The results of characterization observations and hardness testing will be displayed in the form of tables, graphs, and pictures.

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RESULTS AND DISCUSSION

In the Development of Limestone Materials in Mount Branti, Lampung Province, there is a content of 97.43% calcium carbonate (CaCO3) and other elements, including 54.56% Calcium oxide (CaO), 1.68% Magnesium Carbonate (MgCO3), 0.15% Iron Trioxide (Fe2O3), 0.81% magnesium oxide (MgO), 0.03% potassium oxide (K2O), and 0.01% Potassium oxide (K2O). Table 1 shows the chemical composition of local limestone in Lampung Province.

Table 1. Chemical Composition of Limestone Test Results with Chemical Analysis of Beranti Limestone

No	Chemical Composition	Result (%)
1	Calcium Carbonate ($CaCO_3$)	97,43%
2	Magnesium Carbonate(MgCO3)	1,68%
3	Iron Trioxide (Fe_2O_3)	0,15%
4	Magnesium Oxide(MgO)	0,81%
5	Calcium Oxide(CaO)	54,56%
6	Potassium Oxide(K_2O)	0,01%

(Source: Sucofindo, 2022)

FTIR is a tool to determine the type of chemical bonds, including calcium phosphate compounds. FTIR tools are dominated by infrared spectroscopy. The sample to be analyzed uses infrared radiation in the form of powder, which is placed in a place to be irradiated with infrared radiation. Some of the infrared radiation will be absorbed, and some will be transmitted by the sample and forwarded to the computer network for processing. To get the peak pattern of the chemical bond, the tool used is the Nicolet iS50 FT-IR type (Arrafiqie et al., 2016).

Based on the results of the FTIR spectral test using the hydrothermal method, FTIR functions to identify functional groups in the sample. The PO_4^{3-} group bond has the highest intensity (CaO, CO2) at a distance between 4000 and 500 cm^1. Figure 1, the powder that has been through calcination, has a peak group on phosphate (PO43-) detected at a wave vibration of 1025.45 cm^{-1}, Ca-O (calcium oxide) has a distance of 1413.59 cm^{-1}, and the O-H group is at a distance of 3030.33 cm^{-1}. According to Sedyono and Tantowi (2008) phosphate group bonds (PO_4^{3-}) are 1033.8 cm^1, calcium oxide (CaO) is 1404.1 cm^1, and O-H bonds are 3500 cm^1. According to Arrafiqie et al. (2016) the presence of phosphate (PO_4^{3-}) and OH are the functional groups of hydroxyapatite.

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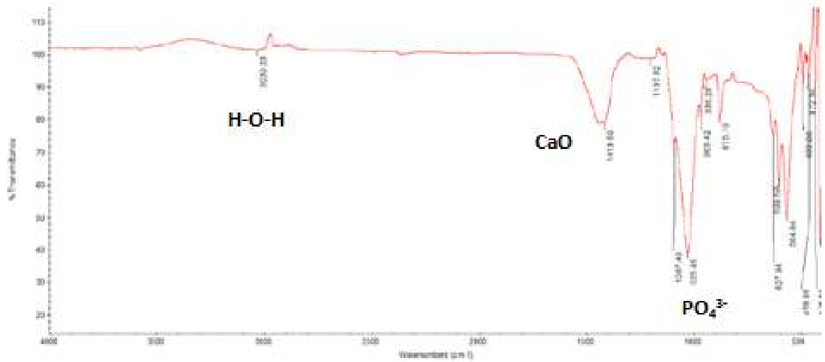

Figure 1. FTIR Pattern 600°C

Figure 1: The powder that has been through calcination has a peak group on the phosphate (PO_4^{3-}) detected at a wave vibration of 1018.57 cm^1, calcium oxide (Ca-O) has a distance of 1422.14 cm^1, oxygen CO_2 has a distance of 2359.90 cm^1, and the H-OH group is at a distance of 3467.40 cm^1, which resembles the FTIR pattern of commercial products. According to Sedyono and Tantowi (2008), phosphate group bonds (PO_4^{3-}) are 1033.8 cm^1, calcium oxide (CaO) is 1404.1 cm^1, and OH bonds are 3500 cm1. According to Arrafiqie et al. (2016) the presence of phosphate (PO_4^{3-}) and OH are the functional groups of hydroxyapatite.

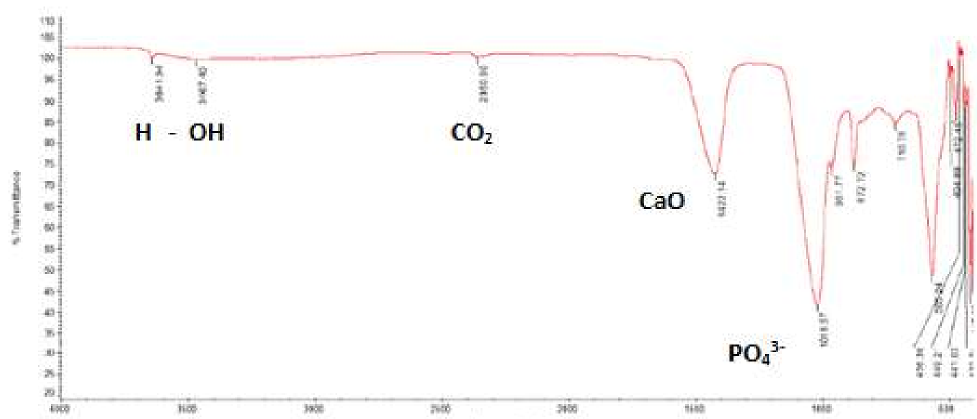

Figure 2. FTIR Pattern 800°C

Figure 2: The powder that has been through calcination has a peak group at PO_4^{3-} (phosphate) detected at a wave vibration of 1016.11 cm^1, Ca-O (calcium oxide) has a distance of 1420.87 cm^1, and the CO_2 group is at a distance of 2360,00 cm^1. According to Sedyono and Tantowi (2008), phosphate group bonds (PO_4^{3-}) are 1033.8 cm^1, calcium

oxide (CaO) is 1404.1 cm1, and OH bonds are 3500 cm1. According to Arafiqie et al. (2016) the presence of phosphate (PO_4^{3-}) and OH are the functional groups of hydroxyapatite. The CO_2 bond has a very low intensity due to the outside air.

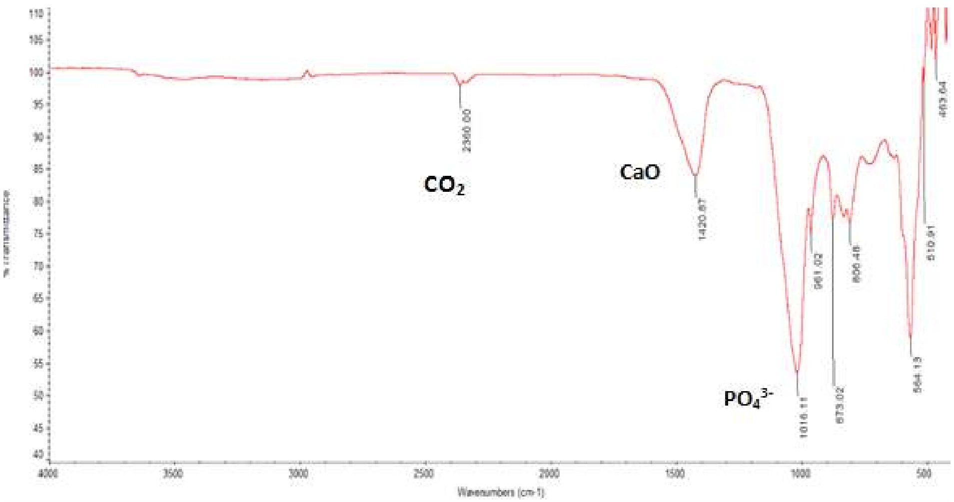

Figure 3. FTIR Pattern 1000°C

XRD characterization aims to determine the crystallinity of the sample based on the 2θ value and based on comparison with commercial data to determine the level of similarity with the local pure powder XRD pattern compounds.

XRD pattern of local natural powder

XRD characterization was carried out to determine the phases contained in the limestone. Qualitative analysis of limestone powder XRD data using Match software. From the matching results, it is known that the limestone samples are dominated by $Ca(CO)_3$ and $Ca(OH)_2$ phases with reference to the diffraction standards ICDD No. 84-1263 for $Ca(CO)_3$ and ICDD No. 47-1743 for $Ca(OH)_2$ with reference to standard hydroxyapatite. The phase formed in local limestone calcite development consisting of calcium carbonate can be used for calcium oxide; it is shown in Figure 18 (Farhani, 2014).

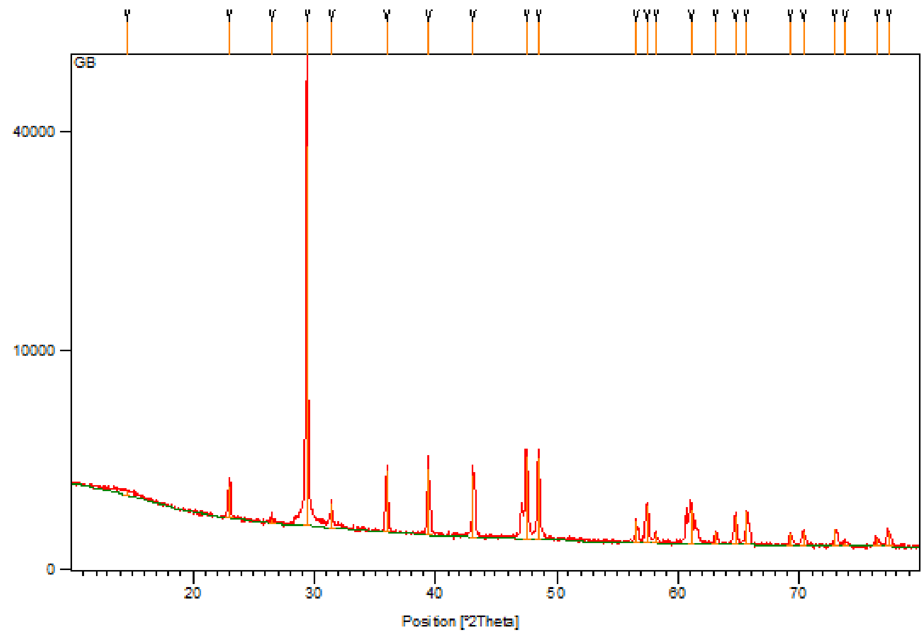

Figure 4. XRD calcination of natural limestone powder in Lampung Province

Figure 4 shows the XRD pattern of locally produced calcite. The highest peak x-ray diffraction pattern has an angle of 2 = 29.38 (100%), which resembles commercial calcite. So local limestone powder can be used as calcite ($CaCO_3$) for hydroxyapatite biochromics. According to Arrafiqie et al. (2016) the X-ray diffraction pattern can be seen at the peak of the calcite characterization with a high intensity at an angle of 2 = 29.38 (Ca); 31.44; 35.97; 39.91; 43,18.

XRD pattern 600°C

The temperature of 600°C shows that the temperature of 600°C has a peak with intensity similar to that of the hydroxyapatite pattern, which has a sharp peak of crystallinity. In this case, Sholehan (2014) said in his research that at a temperature of 600°C, it also has a sharp hydroxyapatite pattern.

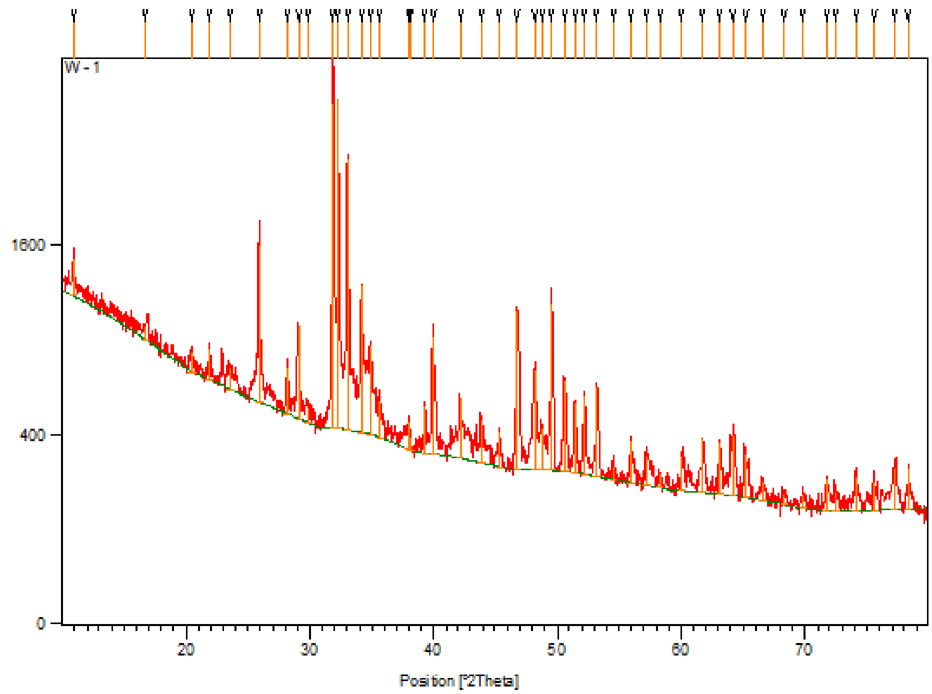

Figure 5. XRD pattern Sintering temperature 600°C

Figure 5 shows the 600°C XRD pattern of local product calcite. The highest peak x-ray diffraction pattern at 100% has an angle of 2 = 32.26 ($CaHPO_4$), 33.03, 34.14, 35.68, and 37.97, which resembles commercial calcite. According to Sedyono and Tantowi (2008) the results that occur can be compared with commercial products (SRM 2910 and HA 2000).

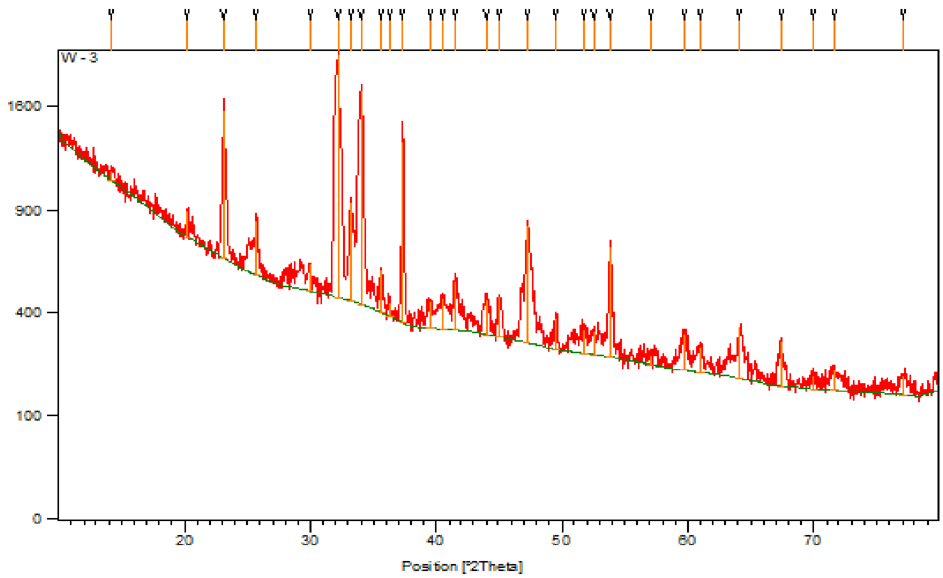

Figure 6. XRD pattern Sintering temperature 800ºC

Figure 6 shows the 800ºC XRD pattern of local calcite. The highest peak x-ray diffraction pattern of 100% has an angle of 2 = 32.15 ($CaHPO_4$), 33.21, 34.00, 35.62, and 36.30, which resembles commercial product calcite. According to Sedyono, J., et al. (2008) the results that occur can be compared with commercial products (SRM 2910 and HA 2000).

CONCLUSION

In this study, the local limestone in Lampung Province contains a calcium carbonate ($CaCO_3$) content of 97.43%. The FTIR pattern of the product produced in this study is similar to that of a commercial product in the sintering process at 600ºC for 2 hours.

The HA powder elements were sintered at 600ºC for 2 hours, showing that the local HA products were similar to imported products in the 2-angle XRD pattern of 32.26. The SEM-EDX characterization showed a morphology similar to bone tissue, whereas for products with sintering parameters of 1000ºC for 4 hours, the microstructural network was more homogeneous. The Ca/P ratio value of 1.4 obtained the hydroxyapatite pattern at a temperature of 1000ºC for 4 hours. The highest vikers hardness was found in hydroxyapatite sintered at 1000ºC for 4 hours.

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