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Original Article

Sintering Behavior of Lampung Limestone-Based Hydroxyapatite for Use as a Bone Filler Material

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Limestone from Mount (Mt.) Beranti, Lampung Province, contains 97.43% calcium carbonate ($CaCO_3$), making it a suitable natural precursor for synthesizing hydroxyapatite (HA). HA is widely utilized as a bone tissue filler, particularly in treating osteoporosis. In this study, $CaCO_3$ was processed using ball milling at 300 rpm for durations of 2, 3, and 4 hours, followed by sintering at temperatures of 600°C, 800°C, and 1000°C for holding times of 2, 3, and 4 hours. FTIR analysis using the hydrothermal method on calcined limestone powder revealed characteristic peaks corresponding to phosphate (PO_4^{3-}) at 1025.45 cm^{-1}, calcium oxide (Ca–O) at 1413.59 cm^{-1}, and hydroxyl (O–H) at 3030.33 cm^{-1}, which closely resemble those found in commercial HA. SEM-EDX analysis at 1000°C for 4 hours showed a homogenous microstructure, with EDX results indicating the highest concentrations of calcium and phosphate after milling for 2 hours. Vickers hardness testing confirmed the highest hardness value was also achieved at 1000°C for 4 hours. Overall, the FTIR, SEM-EDX, and microhardness results demonstrate enhanced properties of HA, supporting its effectiveness as a material for filling porous bone tissue.

Keywords: Limestone; Hydroxyapatite (HA); Calcium Carbonate ($CaCO_3$); Bone Filler

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1. Introduction

Bones are essential components of the human body, functioning to support and protect vital organs, while also playing a role in mineral metabolism, particularly involving calcium and phosphorus. The primary component of bone is hydroxyapatite, a calcium phosphate mineral that provides strength and rigidity. A deficiency in calcium can lead to brittle bones and increase the risk of osteoporosis [1]. Tissue engineering is employed to support bone regeneration, with cells as the key element requiring a suitable environment to differentiate into osteoblasts [2]. The bone matrix is arranged in lamellae with a thickness of 3–7 μm, featuring helical fibers and an interlamellar angle of approximately 90° [3]. Bone can also be described as a composite rod composed of nano-apatite particles (<100 nm) organized within lamellae and bound to collagen [4].

Pure hydroxyapatite (HA), with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, contains two types of calcium atoms in its unit cell. The Ca(2) atoms are surrounded by six oxygen atoms from P–O and OH groups, forming a triangular arrangement along the crystal axis, while Ca(1) is found in an almost octahedral coordination [5]. HA belongs to the Apatite group, which experienced a significant increase in import volume from 2009 to 2012—starting from 5 kg in 2009, rising to 58.5 tons in 2010, 80 tons in 2011, and surging to 1330 tons in 2012 [6].

Hydroxyapatite possesses three key properties as a bone graft material: biocompatibility, allowing it to integrate into the body without triggering an immune response; bioactivity, enabling the formation of a biological apatite layer that bonds directly with bone; and osteoconductivity, supporting the growth and formation of new bone tissue. These properties are influenced by factors such as crystallinity, crystallite size, processing temperature and pressure, and porosity [7].

Limestone forms organically in coastal regions through the sedimentation of biological remains such as shells, snails, algae, animal skeletons, and coral [8]. Natural limestone typically contains around 50% calcium carbonate, along with other components such as carbonate (CO_3), calcium oxide (CaO), magnesium oxide (MgO), silica (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3), as revealed through XRF testing of limestone from Tuban [9].

The sol-gel method is an effective technique for synthesizing nano-phase hydroxyapatite, requiring strict control of pH and temperature. However, this method often involves multiple processing steps and high costs to achieve optimal results [7]. Meanwhile, limestone from Mt. Branti in Lampung Province contains 97.43% calcium carbonate ($CaCO_3$), along with other elements such as 54.56% CaO, 1.68% $MgCO_3$, 0.81% MgO, 0.15% Fe_2O_3, 0.03% K_2O, and 0.01% of other trace components, based on chemical analysis [10].

The complete chemical composition of limestone from Mt. Branti, Lampung Province—which includes 97.43% $CaCO_3$, 54.56% calcium oxide (CaO), 1.68% magnesium carbonate ($MgCO_3$), 0.81% magnesium oxide (MgO), 0.15% iron oxide (Fe_2O_3), 0.03%, and 0.01% potassium oxide (K_2O)—is presented in Table 1 [11].

Table 1. Chemical Composition of Limestone Based on Chemical Analysis Results

No.	Chemical Composition	Percentage (%)
1	Calcium carbonate ($CaCO_3$)	97,43 %
2	Magnesium Carbonate ($MgCO_3$)	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 %

2. Materials and Methods

Limestone chunks were washed using distilled water (aquades) and dried. The dried chunks were then crushed using a hammer and ground into powder particles. The powder was subsequently ball-milled at a speed of 300 rpm for a duration of 2 hours. After milling, the powder was sieved using a 250 μm mesh, producing particles smaller than 250 μm (< 250 μm), and then weighed to 5 grams. The limestone powder was then mixed with a solvent (either distilled water or ethanol) and combined with sodium hydrogen phosphate in the following composition: 5 grams of limestone powder, 5.34 grams of sodium hydrogen phosphate, and 10 ml of distilled water. This mixture was ball-milled again until a wet paste was formed. The paste was then oven-dried for 17 hours. After drying, 3 grams of the sample were weighed for the sintering process. Sintering was carried out at temperatures of 600°C, 800°C, and 1000°C, with holding times of 2, 3, and 4 hours respectively. Compaction was performed at room temperature with a holding time of 5 minutes.

3. Results

3.1. MicroVickers Hardness

Before to the Vickers hardness test, the samples were compacted under a pressure of 5 MPa for 5 minutes for each sintering temperature (600°C, 800°C, and 1000°C) and holding times of 2, 3, and 4 hours. After compaction, the samples were re-sintered according to the specified parameters. Microhardness testing was conducted based on ASTM C1327 standards at five different points, and the results were averaged and presented in Figure 1.

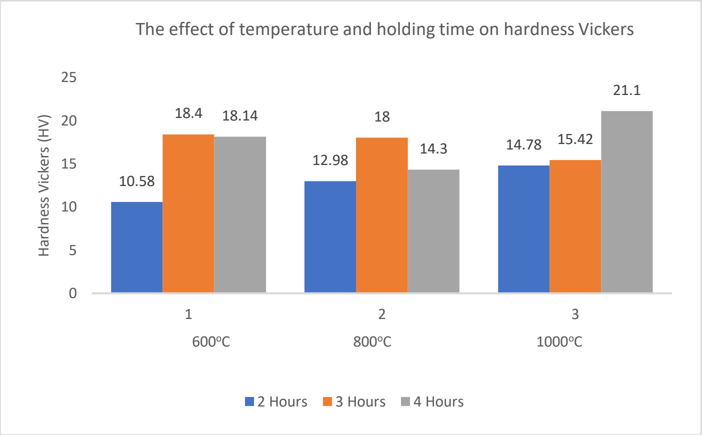

Figure 1. Graph of the effect of sintering and holding time on the hardness of HA (Hydroxyapatite)

Based on the figure, the results of the Vickers hardness test indicate that the increase in temperature and sintering time is directly proportional to the hardness value of local hydroxyapatite (HA). The highest hardness value was achieved at a temperature of 1000°C for 4 hours, reaching 27.1 HV, while the lowest value was obtained at a temperature of 600°C for 2 hours. The increase in sintering temperature and holding time shows structural changes and enhanced bonding between elements, thereby increasing the hardness value at the optimum temperature of 1000°C and a holding time of 4 hours. This is also supported by the SEM analysis data..

3.2. Effect of Variation of Sintering Time and Temperature on Calcium, Phosphate, and Oxygen Content in Local Hydroxyapatite (HA)

Holding time and sintering temperature can affect the composition content of local hydroxyapatite (HA) materials such as calcium, phosphate, and oxygen elements, as explained in Figure 2 below.

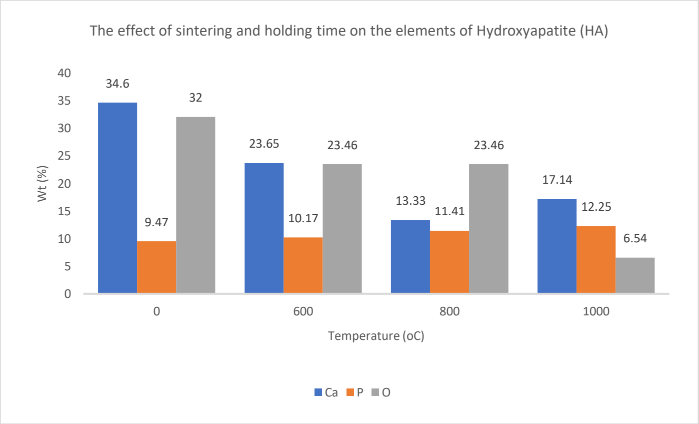

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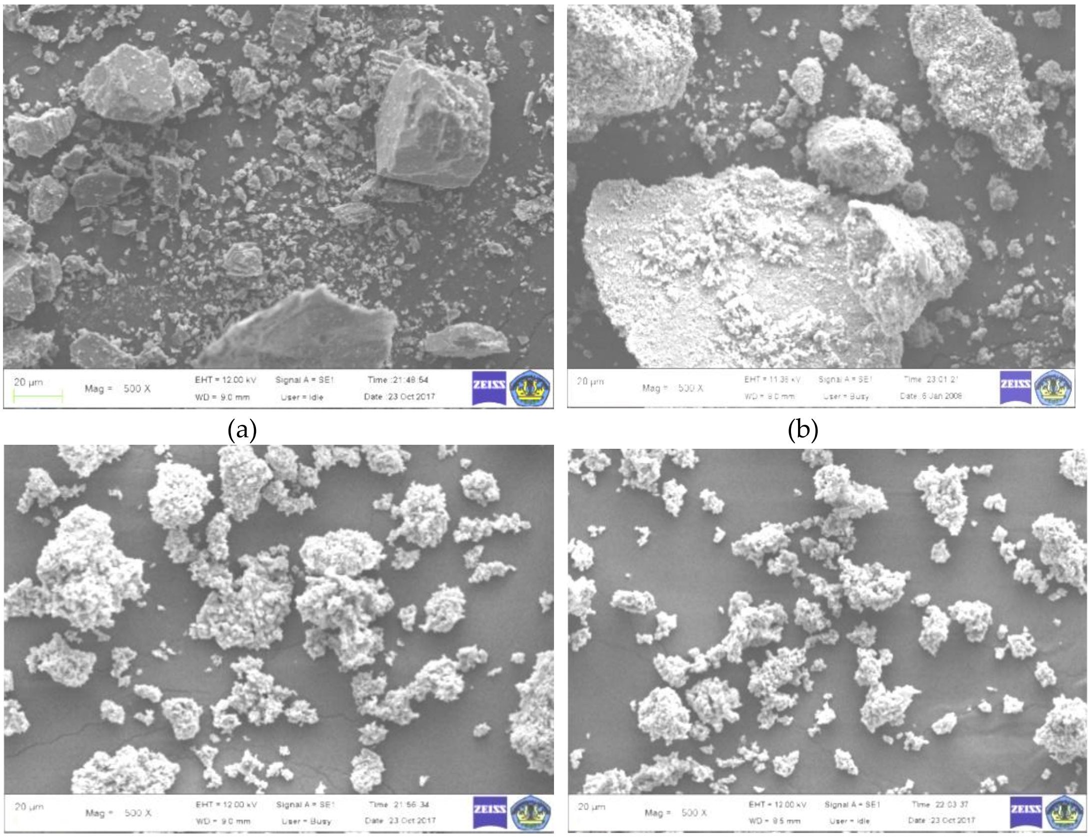
Figure 2. Effect of sintering on the (HA) element of hydroxyapatite

Based on the figure, the initial pure calcium content was 34.46%, but it decreased after the sintering process as the temperature increased. In contrast, the initial phosphate content was lower, but it increased after sintering at 1000°C, reaching 12.25% due to the elevated temperature. The oxygen content prior to sintering was relatively high, approximately 32%, as the material had not yet undergone the heating process [9].

3.3. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) Analysis

The SEM morphology of local limestone powder shows hexagonal and cubic crystal shapes. However, the particle sizes appear non-uniform and irregular, as observed at 500× magnification, shown in Figure 3a. The SEM morphology at a sintering temperature of 600°C for 2 hours reveals powder particles that are not yet homogeneous or fully fused, as seen at 500× magnification (20 µm), shown in Figure 3b. This is due to the relatively low temperature, which results in incomplete water evaporation. The SEM morphology at a milling speed of 300 rpm for 3 hours and a sintering temperature of 800°C for 3 hours shows that the powder particles begin to fuse and become more homogeneous, as observed at 500× magnification (20 µm), shown in Figure 3c. This improvement is attributed to the increased temperature, which facilitates the removal of moisture from the powder. The decrease in elemental content is also associated with the increase in sintering temperature from 600°C for 2 hours to 800°C for 3 hours. The SEM morphology at a sintering temperature of 1000°C for 4 hours shows a higher degree of particle homogeneity compared to the samples sintered at 600°C for 2 hours and 800°C for 3 hours, as shown in Figure 3d.

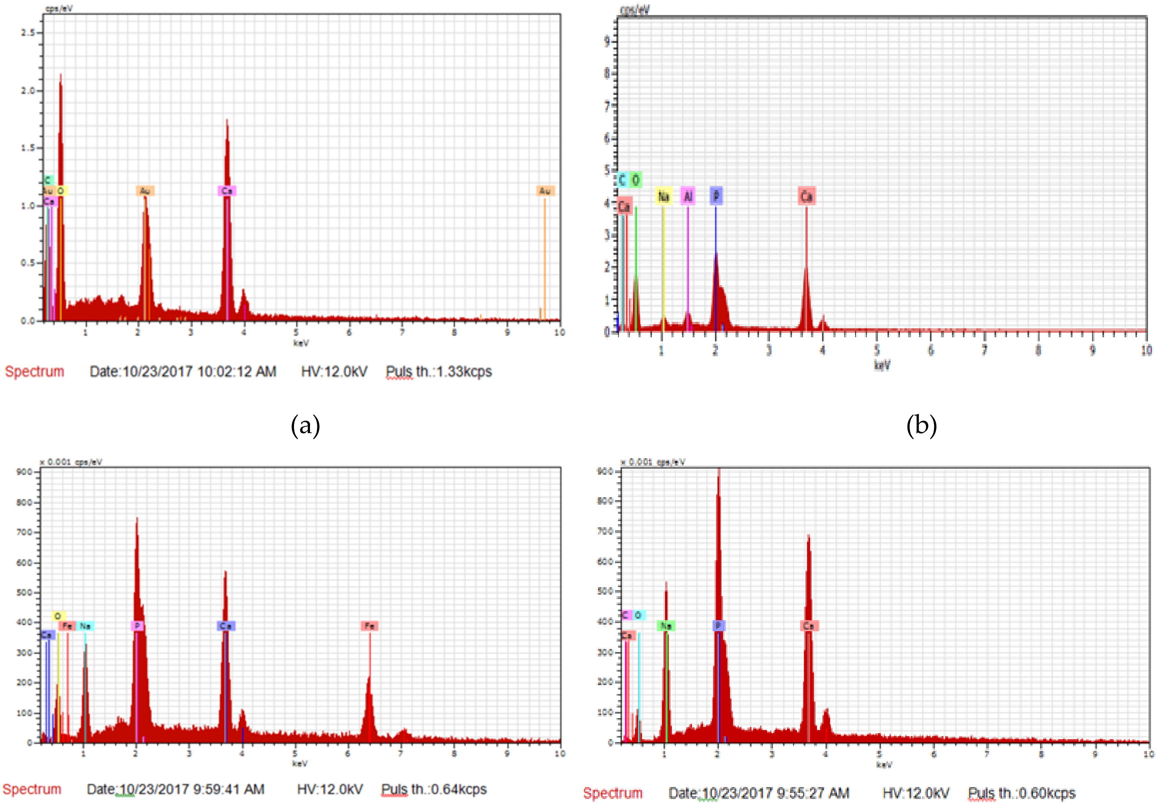


(a) (b)

. (c) (d)

Figure 3. SEM morphology 500x (a) Local limestone powder, (b) Sintering 600°C for 2 hours, (c) Milling speed 300 rpm for 3 hours with sintering temperature 800°C for 3 hours, (d) sintering 1000°C for 4 hours

While SEM is used to observe the microstructure of material's structure, the EDX is employed to analyze the chemical composition of the sample. The EDS system consists of four main components: an X-ray source, an X-ray detector, a pulse processor, and an analyzer. A scanning electron microscope is equipped with a cathode and magnetic lenses to generate and focus the electron beam, and since the 1960s, it has supported elemental analysis. The detector converts X-rays into voltage signals, which are then processed and analyzed to produce elemental composition data.



(a) (b)

(c) (d)

Figure 4. EDX graph on (a) Local limestone, (b) Sintering 600°C for 2 hours, (c). Sintering 800°C for 3 hours, (d) Sintering 1000°C for 4 hours

The EDX analysis identified the main elemental contents as calcium (Ca) 34.46%, oxygen (O) 32.00%, carbon (C) 9.47%, and gold (Au) 17.99%. The EDX analysis at 600°C for 2 hours revealed elemental compositions of Ca 23.65%, O 23.46%, C 2.44%, and P 10.17%. At 800°C for 3 hours, the analysis showed elements with the following compositions: Ca 13.33%, P 11.41%, Na 10.11%, O 6.00%, and Fe 15.29%. At 1000°C for 4 hours, the EDX results identified elements with the following compositions: Ca 17.44%, P 12.25%, Na 14.87%, O 6.54%, and C 0.51%. The calcium content was relatively lower compared to the sample sintered at 600°C for 2 hours.

3.3. Fourier Transform Infra Red (FTIR) Results

Based on the FTIR spectral results using the hydrothermal method, this technique is utilized to identify functional groups within the sample. The highest intensity peak originates from the phosphate (PO_4^{3-}) group, followed by CaO and CO_2, within the spectral range of 4000–500 cm^{-1}.

In the sample sintered at 600°C, the calcined powder shows a PO_4^{3-} vibrational peak at 1025.45 cm^{-1}, a Ca–O peak at 1413.59 cm^{-1}, and an O–H peak at 3030.33 cm^{-1}. Reference values for phosphate, calcium oxide, and hydroxyl groups are 1033.8 cm^{-1} (PO_4^{3-}), 1404.1 cm^{-1} (CaO), and 3500 cm^{-1} (O–H), respectively. The presence of PO_4^{3-} and OH groups is a key functional characteristic of hydroxyapatite. In the sample sintered at 800°C, the calcined powder exhibits functional group peaks resembling those of commercial FTIR patterns, with PO_4^{3-} at 1018.57 cm^{-1}, Ca–O at 1422.14 cm^{-1}, CO_2 at 2359.90 cm^{-1}, and O–H at 3467.40 cm^{-1}. The reference peaks—PO_4^{3-} (1033.8 cm^{-1}), CaO (1404.1 cm^{-1}), and OH (3500 cm^{-1})—confirm the functional group identity of hydroxyapatite [10, 11].

In the sample sintered at 1000°C, the phosphate group (PO_4^{3-}) was detected at 1016.11 cm^{-1}, Ca–O at 1420.87 cm^{-1}, and CO_2 at 2360.00 cm^{-1}. The presence of PO_4^{3-} and OH groups remains a distinctive signature of hydroxyapatite. The low intensity of the O_2 signal is likely due to environmental air interference during analysis.

4. Discussion

Vickers Hardness Testing shows that an increase in sintering temperature and time is directly proportional to the hardness value of the local hydroxyapatite (HA). The highest hardness value was achieved at 1000°C for 4 hours, reaching 27.1 HV, while the lowest value was obtained at 600°C for 2 hours. The increase in hardness is influenced by the higher sintering temperature and holding time, which enhance the bonding between elements. As the sintering temperature increases, the phosphate content rises to 12.25% at 1000°C; however, the oxygen content decreases to 6.54% at 1000°C, and the calcium content drops to 17.14% at 800°C.

At higher sintering temperatures, the HA crystal structure becomes more stable and organized. This allows phosphate ions (PO_4^{3-}) to form stronger bonds within the crystal lattice, thereby increasing the intensity or concentration of phosphate. Furthermore, the decomposition of impurities or volatilization of other compounds may also increase the relative proportion of phosphate in the sample. Calcium may undergo volatilization or migration during sintering, especially at high temperatures. Some calcium compounds may react to form other phases like CaO or even escape from the system, leading to a reduction in calcium content within the HA structure. The imbalance in the Ca/P ratio can also indicate structural degradation of HA at higher temperatures. A decrease in oxygen content may occur as hydroxyl (OH^-) groups in HA undergo dehydroxylation at high temperatures, releasing water (H_2O) that evaporates. This process reduces the oxygen content within the structure. Additionally, an increase in crystallinity can lead to greater stability or loss of oxygen-containing functional groups, as also mentioned elsewhere [12].

This is supported by FTIR data, where the presence of phosphate (PO_4^{3-}) and OH groups is characteristic of hydroxyapatite. The phosphate group is detected at 1033.8 cm^{-1}, CaO at 1404.1 cm^{-1}, and OH at 3500 cm^{-1}, with a very low intensity O_2 signal, which is caused by the influence of ambient air affecting the oxygen concentration.

5. Conclusions

Vickers Hardness Test results indicate that the increase in sintering temperature and time is directly proportional to the hardness value of the local hydroxyapatite (HA). SEM Morphological Analysis of sintering at 1000°C for 4 hours shows that the powder grains have a better degree of homogeneity compared to those sintered at 600°C for 2 hours and 800°C for 3 hours. This is due to the higher temperature helping to remove water vapor from the powder. With an increase in sintering temperature, the phosphate content increases to 12.25% at 1000°C, while the oxygen content decreases to 6.54% at 1000°C, and calcium content drops to 17.14% at 800°C. These findings from EDX analysis are supported by FTIR data. The results from FTIR, SEM-EDX characterization, and Vickers microhardness tests demonstrate an improvement in the properties of HA with the increase in sintering temperature to 1000°C for 4 hours. This process represents the optimal parameters for the limestone from Mt. Beranti, Lampung Province, which contains 97.43% calcium carbonate ($CaCO_3$), a primary material for the production of Hydroxyapatite (HA), serving as a key material for filling porous bone tissue.

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