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Synthesis And Characterization Carbonate Apatite From Bukit Tui Limestone, Padang, Indonesia

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ABSTRACT

Carbonate apatites has been synthesized using Bukit Tui limestone and investigated by XRD, FT-IR, Nanolaser, TGA, and SEM. In present study, PCC was mixed with gypsum was treated with 1M $(NH_4)_2HPO_4$*. In visual observations, showed that same colour morphologycally before and after treated with 1M* $(NH_4)_2HPO_4$*. XRD analysis revealed that formed carbonate apatite A-type and B-type FT-IR analysis appears band absorption at 1120* cm^{-1} *(P-O stretching), 460, 560-600* cm^{-1} *(P-O bending), and 1450,1410, and 876* cm^{-1} *(C-O stretching). Nanolaser characterized the change of particle size after treated by phospate salt. TGA analysis showed that stability of material obtained depending on compositions and SEM images showed that well distributed of particles.*

Keywords: limestone, precipitated calcium carbonate, carbonate apatite.

INTRODUCTION

West Sumatra as one of the province in Indonesia has natural resources which is adequate as coal, limestone and petroleum. Limestone is the one of natural resources that has not received attention from the Government. This deposit of limestone achieves 2 trillion tons that distributes in Muara Kiway, Pasaman Regency, Subdistrict Halaban Luhak 50 Kota, Tanjung Gadang, Sijunjung Regency, Bukit Tui Padang Panjang and Subarang, Solok Regency.

Limestone is a mineral that occurs naturally and is widespread in nearly all the world. The largest component contained in limestone is calcium and carbonate which is generally joined to form calcium carbonate ($CaCO_3$). Most people use limestone with modest knowledge, knowledge is limited only as quicklime, limestone pairs and raw materials so that the cement industry is still low economic value. Therefore the need for efforts to increase the value of product quality limestone to process them into products that are more efficient in the industry as precipitated Calcium Carbonate (PCC)[1]. In previous studies utilizing limestone for the manufacture of PCC (Precepitated Calcium Carbonate), which has economically high value [2]. With a high degree of purity may be established in the nanoparticle size, the PCC can be used as a basic materials in the formation of hydroxyapatite and carbonate apatite which is widely used in the health sector such as the replacement of implant fractures and broken bones. The

Decade last seen in the process of replacement of damaged bone-many used hydroxyapatite, but hydroxyapatite has a major weakness, which Hydroxyapatite can not be completely absorbed by the body, so in the long term hydroxyapatite will be found in the body. One of the the weaknesses of hydroxyapatite is having low mechanical fragility and strength [3].

Replacement of hydroxy group by carbonate, will lead the change of structure and morphology of apatite and biological reactivity that will increase of bone mineral [4]. In addition, carbonate apatite can be reabsorbed by osteoclasts and replaced with new bone, stable in physical conditions and thermodynamics [3,5-8].

MATERIALS AND METHODS

Materials and Equipments: The equipment used were some glassware, autoclave (hydrotermal vessel), the analytical balance (Kern ALJ 220-4 m), plastic molds, hot plate stirrer, petridish, pH paper, oven, furnace, crusher (Pulverisette 16-Fritsch), CO_2 gas cylinder and the desiccator. The instruments were the Size and Shape Analysis Nano Laser (Analysette 22 NanoTec Plus Fritsch), XRD, SEM (Philips Analytical), FTIR (Jasco FT/IR 460 Plus), TGA (Leco TGA 701), and XRF (Arl 9800 xp, Simultaneous). (Brataco), diamonium hydrogen phosphate $(NH_4)_2HPO_4)$ (Merck), nitric acid 2M (HNO_3) (Merck), ammonium hydroxide (NH_4OH) (Brataco), filter paper Whatman 42 and water distillation.

Procedure: Limestone was grinded in crusher with 90 mesh, then analyzed using XRF. Sample was calcined in furnace for 5 h at 900°C and was cooled. 16.8 g of metal oxide obtained was dissolved in 300 mL of 2M HNO_3 and stirred for 30 min, then filtered. To the filtrate was added at 60^oC NH_4OH solution till pH 12 reached. The solution was filtered and flowed gas CO_2 at pH 8. The sediment formed filtered and washed by aquadest, dried at $100\text{-}115^0C$ for 1 h. The mixture of 3 g of gypsum and obtained PCC with variations 0, 10, 25, 50, 75, 90, 100% of the weight gave code G100P0, G10P90, G75P25, G50P50, G25P75, G90P10, G0P100. The mixture was put into aquadest and formed into mold. The mold was placed in a petridish closed at room temperatures for 24 h and then followed soaking in autoclave which contains 81.6 mL solution of 1M $(NH_4)_2HPO_4$ at 100°C for 24 h. The specimens are removed from the solution, washed by aquadest, dried for 24 h. The resulting product is analyzed by Size and Shape with the Nano Laser, FTIR, XRD, TGA, SEM.

RESULTS AND DISCUSSION

Results of the analysis of the content of the limestone Bukit Tui Padang Panjang, West Sumatra showed in table 1 as below.

Table 1. The XRF analysis of Bukit Tui Limestone, Padang Panjang

Compound	Composition (%)
SiO_2	4,16
Al_2O_3	1,78
Fe_2O_3	0,53
CaO	50,56
MgO	1,62
LOI	41,35

XRF analysis showed that content CaO in limestone more 50 % and it can be used as raw material in synthesis PCC to form carbonate apatite. According to Jamarun et al [1] the best quality PCC has CaO more than 50 % in limestone and using carbonation method.

Formation Carbonate Apatite from PCC: Formation Carbonate apatite with 6 variations PCC-gypsum blocks that can be mold and good formed.The sample codes G100P0, G90P10, G75P25, G50P50, G25P75, G10P90 and only 1 block variations that could not be formed, i.e. G0P100. On a composite with code G0P100, the absence of gypsum block due to could not be established because if PCC 100% block content can't be mold because the PCC does not have the adhesives properties.

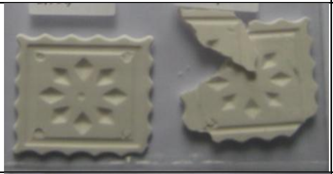
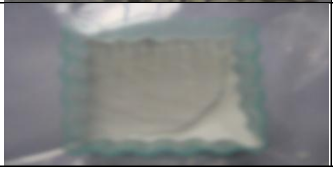
Sample	Before Soaked	After Soaked	Colour
G100P0			+++++++
G90P10			++++++
G75P25			+++++
G50P50			++++
G25P75			+++
G10P90			++
G0P100		-	+

Fig 1. Observation of Color Blocks PCC-Gypsum before and after soaked in a solution 1M $(NH_4)_2HPO_4$.

Macroscopically morphological observation, also did not show the color difference between PCC-gypsum blocks before and after being soaked in a solution of 1M $(NH_4)_2HPO_4$. This suggests soaking in a solution of phosphate salts do not affect changes of gypsum block PCC. Fig. 1 showed that the more the content of PCC in the sample will create a more bright color blocks due to color of the PCC, formed, whiter than the gypsum.

Analysis Nano Laser: Resulted distribution size particle by nano laser showed in figure 2.

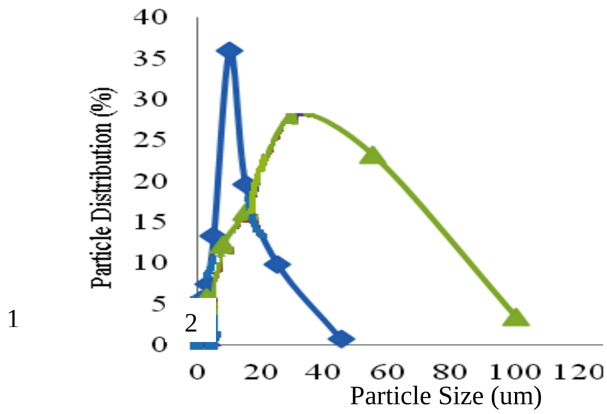


Fig 2. Comparison of particle size distribution and with code G25P75 and G25C75 before the soaked G25P75A and after soaked in a solution of 1M $(NH_4)_2HPO_4$; (2)G25P75B

Based on fig 2, can be seen on G25P75 particle size range 0.1-45 µm which 30% dominantly consisting of 10 µm particle size. The sample code of G25P75 size range 1-300 µm which consist of 30.4% by 70 µm particle size. In G25P75B, the sizes of particles are in range 0.1-100 µm where commontly consist of 28.1% by 30 µm size of particle. Fig. 2 also showed that the process of soaking in solution 1M $(NH_4)_2HPO_4$ could affect the size of particles. In G25P75 there are differences sizes of particles sample before and after phosphatic soaked in saline solution. Block with treatment before soaked distribution particles having smaller than blok which has been soaked in phosphatic saline solution. In generally, can be explained that particles with small size having broad a wide surface will more readily reacting compared with particle having narrow surface.

Fourier Transformation Infra Red (FTIR) Results: The results of FTIR analysis Carbonate Apatite were shown in Fig. 3

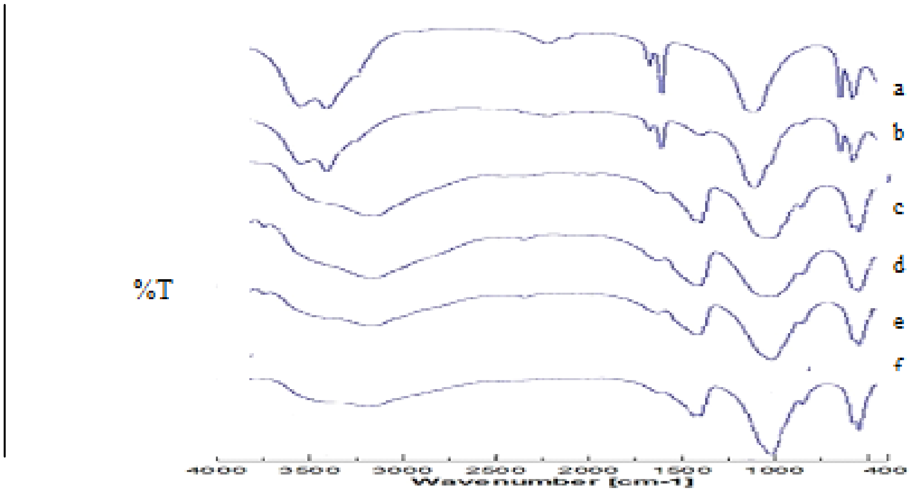


Fig 3. FTIR spectra of carbonate apatite a. G100P0; b. G90P10 c. G50P50 d. G75P25;; G25P75; e. f. G10P90

Fig.3 shows the G100P0 and G90P10 vibration peak of S-O stretching from SO_4^{2-} on 660-670 cm^{-1}. This result due to content of gypsum ($CaSO_4.2H_2O$) was dominant in the composition of the compound. Furthermore, the reduced content of gypsum on the composite, S-streching vibration peak O will be increasingly diminished/lost, which can be seen in the spectra of samples with codes G75P25, G50P50, G25P75, G10P90. The FTIR spectra of compounds demonstrating the appearance of the peak P-O in PO_4^{3-}, and C-O in the CO_3^{-2}(carbonate). The peak P-O vibration of streching coming from PO_4^{-3}at wavenumbers 1120 cm-1, P-O bending vibration is on 460, 560-600 cm^{-1}(3,5) Peak on a wave number 1410, 1450, and 876 cm-1 indicating the vibration of the C-O streching. In addition there are doublet peak in 3400-3500 cm^{-1} area which indicate N-H come from NH^{4+}[6,7]. The results of FTIR analyses showing formation of apatite compounds due to vibration P-O peak from PO_4^{3-} and C-O vibration from CO_3^{-2}(carbonate). C-O vibration peak come from CO_2^{-3} in 876, 1410, 1450 cm-1 indicate existence of carbonate apatite in (CO_3Ap) B-type. This result supported by previous report. The peak of P-O vibrations coming from the partially PO_4^{-3} indicates that the CO_3^{-2}(carbonate) in CO_3Ap has been replaced by the ion PO_4^{-3} after the blocks are soaked in a solution of 1M $(NH_4)_2HPO_4$. Based on the FTIR results, all of samples showed that the carbonate apatite compounds that form is carbonate apatite-type B. This is evidenced from the process of the formation of these compounds is carried out not at too high a temperature 100 ° C, which corresponds to the literatur explained that the formation of carbonate apatite compounds worked at low temperatures will produce carbonate apatite-type B.[5,8].

Thermal Gravimetry Analysis (TGA) Analysis: The TGA analysis in fig. 5, indicated decreasing of weight in all of samples. At 100^oC sample weight reduction caused by evaporate molecules of water that exists on the surface of samples or the loss of the O-H bond. The reduction of weight in G100P0 were 4,15%; G90P10= 4,66%; G75P25=10,35%; G50P50=8.75%; G25P75=8,04%; and G10P90= 4,24% respectivelly. On temperature 200-400 C were release water hydrates, organic groups. The organic groups are expected to come from phosphate ions (PO_4^{-3}). On the samples with code G100P0 in the temperature range of 200-400 C weight reduction of 10,31%; G90P10 of 7,88%; G75P25 of 9,37%; G50P50 of 6,42%; G25P75 of 7,60% respectively. For G10P90, weight reduction of 1.8%. At temperatures higher than 400^0C which is $500\text{-}1000^0C$, showed that at 500^0C carbonate ions CO_3^{-2} is already starting decomposition because calcination CO_2 caused by the sample containing $CaCO_3$ which when heated at temperature up to 1000^0C would release CO_2 gas.(7)

Reduction of weight of each sample vary in the range of temperature.In G100P0, weight reduction only occurs for 0,73% because in this sample does not contain calcium carbonate, which can also be seen from the figure that the compound stable at $400\text{-}1000^0C$. Meanwhile, reduction of weight occur in $500\text{-}1000^0C$. In G90P10 weight reduction was 3,11%; G75P25 was 3,92%; G50P50 was 9,82%; G25P75 was 3,69%; 4.88% is G10P90 code. Additionally, in G10P90, TGA figure showed that these compounds are quite stable. Based on the overall graphic TGA some variation samples analyzed show that differences in the composition of the sample causes the difference in stability. This is because the composition of calcium carbonate as one of the precursors in the sample are also different.

X-Ray Diffraction (XRD) analysis: The crystallite size of the sample can be calculated by using the Debye-Scherrer formula. By measuring the FWHM (Full Width at Half Maximum) of the highest peak of the reflection, the crystal size could be obtained crystalline material. The result of XRD pattern can be compared with the JCPDS 35-180 for the A-type carbonate apatite and carbonate apatite JCPDS 19-0272 for the type-B. Fig. 5 shows the XRD pattern of the sample with code G25P75 after immersion in a solution of $(NH_4)_2HPO_4$ 1M for 24 hours. Three peaks with high intensity, ie at 2θ = 31,775; 32,205; 32,935 each peak has an intensity of 100%, 58.2%, 72.2%. The peak at 2θ = 31,775 and 32,935 is the culmination of crystalline hydroxyapatite (HAp) (JCPDS = 24-0033). The presence of carbonate apatite crystals of type-A is characterized by the appearance of a peak at 2θ = 16.865 (130); 25,935 (002); and 39,765 (013). Meanwhile, the peak at 2θ = 28,185 (102); 32,205 (112); 45,290 (203) and 51,195 (321) signifies the emergence of carbonate apatite crystals of type-B in this sample with a lower intensity. Based on calculations using the Debye equation-Schrrer, crystal size obtained for samples with code G25P75 43.05 nm. XRD results show the obtained hydroxyapatite, carbonate apatite A-type and B-type carbonate apatite [9,10].

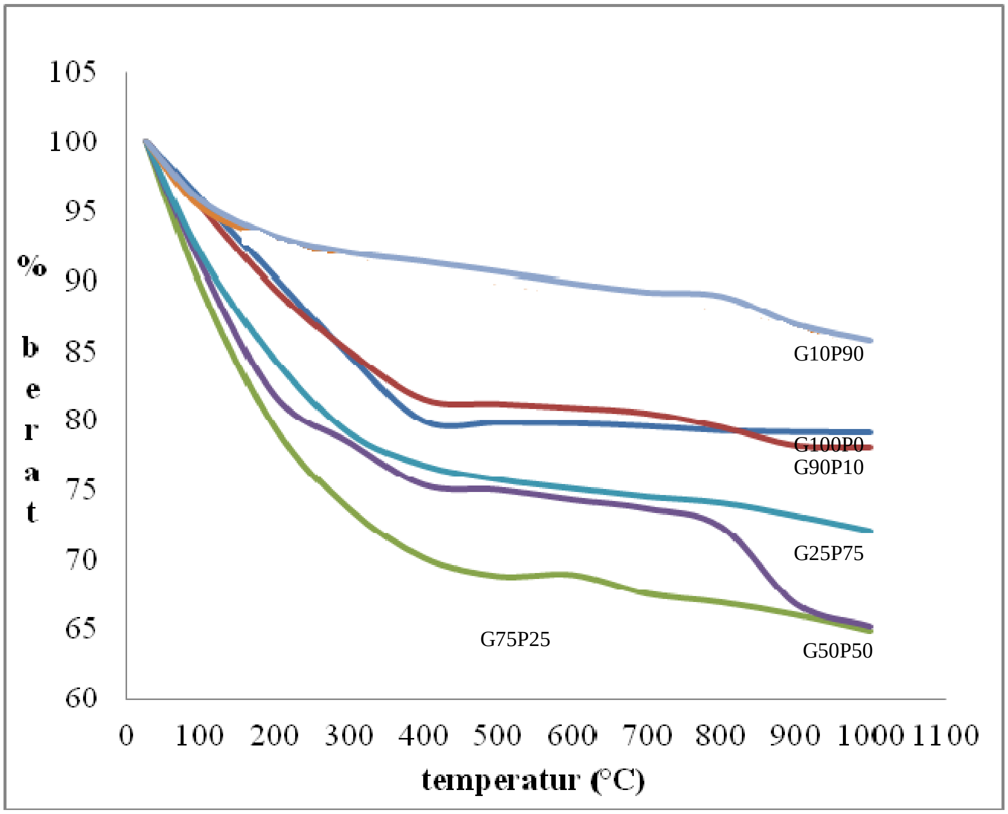


Fig 4. Termogram of TGA carbonate apatitet with variation precursor

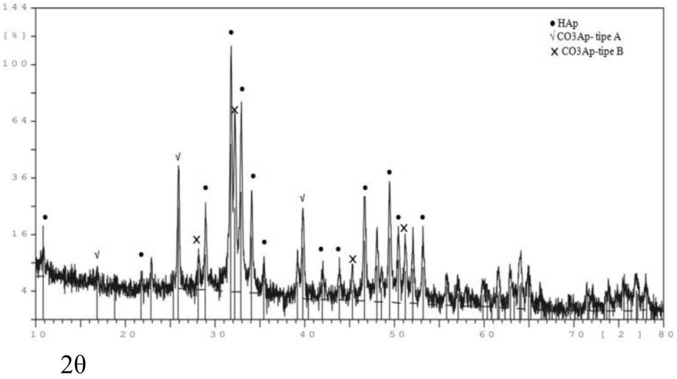
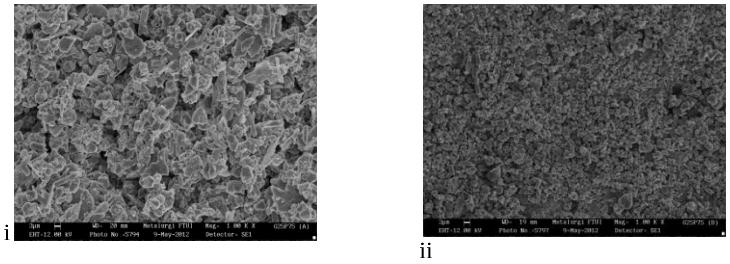


Fig.5. XRD diffractogram of carbonate apatite G25P75

Scanning Electron Microscopy (SEM) Analysis: The samples were analyzed by SEM that samples G25P75 before and after treatment with soaked in a solution of $(NH_4)_2HPO_4$ 1 M for 24 h.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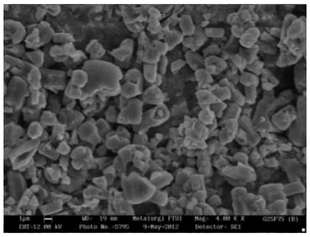

iii

Fig.6. SEM image of G25P75 before soaked (i) and after soaked in a solution of $(NH_4)_2HPO_4$ 1 M for 24 h. (ii) and (iii) 1000 x magnification magnification 4000x

SEM analysis in fig.6 showed that the rather difference between samples G25P75 Fig. 6(i) with the sample before treatment are soaked in a solution of 1M $(NH_4)_2HPO_4$ for 24 h and have best distribution. Particle size of G25P75 ranges between 0.33 - 8.33 μm. Fig. 6 (ii) shows the morphology of SEM samples with G25P75 after soaked in a solution of 1M $(NH_4)_2HPO_4$ the particle became more refined and its spread evenly. Visible difference that particle size samples G25P75 after soaked more refined than before and soaked from Fig. 8(i) and (ii) can be seen evenly spread. Based on Fig. 6(iii) particle distribution quite evenly and plate shape. In magnification 4000x showed taht clearly difference between samples. In 4000x magnification, particle size of G25P75 is 0.33-4.8 μm.

CONCLUSIONS

Based on research that natural limestone that has been processed into PCC and mixed with gypsum can be used as a precursor in the formation of carbonate apatite compounds.The formation of apatite compounds are more easily shaped in the form of block. FTIR spectra analysis and XRD analysis results indicate the formation of carbonate apatite compounds. Size and Shape Analysis showed that the distribution of Laser Nano particle composite G25P75 was 0.1-45 μm before soaked and after soaked in a solution of $(NH_4)_2HPO_4$ 1 m 1-300 μm. TGA analysis showed differences in the composition of the sample causes the thermal stability of these compounds berbedat. The SEM analysis based on the results obtained 0.33 - 8.33 μm and well distributed.

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