International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.
© 2025 Scholar AI LLC.
https://ijpsat.org/
Vol. 51 No. 2 July 2025, pp. 248-255

B-TCP Synthesis Using Calcium From Calcined Paphia Undulata Shells

[1]NYA DANIATY MALAU

[1]Physics Education Study Program
Universitas Kristen Indonesia
Indonesia
Corresponding Author: malaunyadaniaty@gmail.com

Abstract–β-Tricalcium phosphate (β-TCP) is a promising ceramic biomaterial for bone tissue engineering due to its enhanced biodegradability and osteoconductivity compared to hydroxyapatite. This study synthesized β-TCP using a natural calcium source—Batik clam shells (*Paphia undulata*)—via precipitation followed by calcination (900°C, 8 hours). XRD analysis confirmed the formation of β-TCP (67.9%) with a trigonal structure (*a* = 10.4352 Å, *c* = 37.4029 Å), alongside β-calcium pyrophosphate (β-$Ca_2P_2O_7$; 32.1%), attributed to incomplete thermal conversion. SEM revealed agglomerated β-TCP particles (0.5–1.5 µm) with a rough surface morphology. The results highlight the viability of Batik clam shells as a sustainable calcium source for β-TCP synthesis, though further optimization is required to achieve higher phase purity and morphological uniformity. This work advances the development of locally derived biomaterials for biomedical applications.

Keywords: β-tricalcium phosphate, Batik clam shells, precipitation, XRD, SEM, biomaterial

I. INTRODUCTION

Bone is a biological composite material primarily composed of hydroxyapatite (HA) mineral and an organic collagen matrix. With the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, HA serves as the principal mineral phase of bone. Due to its structural and compositional similarity to natural bone mineral, HA is widely recognized as a highly biocompatible and bioactive biomaterial, making it the material of choice for various biomedical applications, particularly in bone tissue engineering and bone defect repair [1]. Its advantages include the ability to directly bond with host bone tissue without eliciting adverse immune responses. However, despite these benefits, HA exhibits significant limitations regarding its extremely slow biodegradation and resorption rates in vivo. When used as implants, HA tends to persist in the body for extended periods, potentially remaining permanently. This persistence may interfere with the natural bone remodeling process where damaged bone is gradually replaced by new, healthy tissue. Consequently, complete integration with new bone and functional regeneration may be compromised, limiting its application in clinical conditions requiring implants that can progressively dissolve and be replaced by new bone over time.

β-Tricalcium phosphate (β-TCP) represents another calcium phosphate ceramic material that demonstrates biocompatibility, osteoconductivity, and crucially, faster biodegradation rates compared to HA [2,3]. These properties enable β-TCP to gradually dissolve and be replaced by new bone during the healing process, making it a promising candidate for resorbable bone implants.

The synthesis of β-TCP can be achieved through various methods including precipitation, solid-state reactions, and sol-gel processes, utilizing diverse calcium and phosphate sources [4]. To date, β-TCP has been successfully synthesized from both natural and synthetic calcium sources. Synthetic calcium sources typically consist of inorganic calcium salts such as calcium nitrate ($Ca(NO_3)_2$), calcium hydroxide ($Ca(OH)_2$), or chemically prepared calcium oxide (CaO) [5]. For natural calcium sources, numerous studies have utilized calcium carbonate ($CaCO_3$)-rich biological waste materials including mollusk shells (e.g., green mussel shells (Perna viridis) [6], rangga clam shells [7], pearl oyster shells [8]), chicken eggshells [9], limestone [10], or coral [11]. In β-TCP synthesis, these calcium sources are reacted with phosphate sources, typically phosphoric acid (H_3PO_4) or phosphate salts such as diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) [4].

The abundance and cost-effectiveness of natural calcium sources are key considerations for economical and sustainable β-TCP synthesis. As a maritime nation, Indonesia possesses significant potential for utilizing shell waste. Clam shells, including Batik clam shells (Paphia undulata), consist primarily of calcium carbonate ($CaCO_3$) in aragonite or calcite forms, which can be calcined to produce pure calcium oxide (CaO) [12]. The resulting CaO can then serve as a calcium precursor for β-TCP synthesis. Utilizing this shell waste not only addresses environmental concerns but also provides a sustainable, value-added alternative raw material for biomedical applications.

Previous studies have successfully synthesized β-TCP from various natural calcium sources. For instance, Susanti and Pradana (2018) synthesized β-TCP from green mussel shells (Perna viridis) [6]. Lestari and Setyarini (2019) also demonstrated the potential of rangga clam shells as a calcium source for β-TCP synthesis [7]. Similarly, Rahayu et al. (2020) investigated β-TCP synthesis from pearl oyster shells [8]. These studies confirm the feasibility of using shell waste as alternative calcium sources for biomaterial synthesis.

Nevertheless, studies specifically investigating β-TCP synthesis using calcium derived from calcined Batik clam shells (Paphia undulata) remain limited. Most previous research has focused on other shell types. Batik clam shells may possess slightly different compositions and structures that could influence the characteristics of the resulting CaO and ultimately, the phase and morphology of the synthesized β-TCP. Therefore, the research gap lies in the insufficient exploration of Batik clam shells (Paphia undulata) as a calcium source for β-TCP synthesis and comprehensive characterization of the resulting product.

This study focuses on synthesizing β-TCP using calcium derived from calcined Batik clam shells (Paphia undulata). This approach is expected to provide novel insights into utilizing marine waste as raw material for biomaterial production while exploring the characteristics of β-TCP derived from natural precursors. The research will investigate how synthesis conditions affect the phase, crystallinity, and morphology of the resulting β-TCP. Characterization will include X-ray diffraction (XRD) for phase identification and crystallinity analysis, along with scanning electron microscopy (SEM) for surface morphology examination. The ultimate objective is to produce β-TCP with optimal characteristics for bone tissue engineering applications.

II. MATERIAL AND METHOD

This study will be conducted through several key stages: raw material preparation, β-TCP synthesis, and material characterization. The detailed methodology is as follows:

A. Preparation of Calcium Oxide (CaO) from Batik Clam Shells and Phosphate Source

Batik clam shells (Paphia undulata) will be collected and thoroughly washed with running water to remove dirt, residual flesh, and other adhering organisms. The shells will then be soaked in deionized water for 24 hours and rinsed again to ensure complete cleanliness. Dried shells will be mechanically crushed using a mortar and pestle to obtain coarse powder. The shell powder will be calcined in a furnace at 900°C for 9 hours to decompose calcium carbonate ($CaCO_3$) into calcium oxide (CaO) and carbon dioxide (CO_2) gas. The calcination process will be carefully controlled to ensure complete conversion of $CaCO_3$ to CaO. The resulting CaO powder will be immediately stored in a desiccator. The phosphate source will be diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) with pro-analysis grade purity. The phosphate solution concentration will be adjusted to achieve the desired Ca/P molar ratio for β-TCP synthesis.

B. *Synthesis of β-Tricalcium Phosphate (β-TCP)*

β-TCP will be synthesized through the wet precipitation method, known for its effectiveness in producing calcium phosphates with controlled stoichiometry. Exactly 2.83 grams of calcined CaO powder will be dissolved in deionized water to form a calcium hydroxide ($Ca(OH)_2$) suspension/solution. This process will be conducted slowly with constant stirring to ensure uniform dissolution, resulting in a 1.2 M calcium hydroxide solution. The pre-weighed $(NH_4)_2HPO_4$ will be dissolved in deionized water to prepare a 0.8 M phosphate solution.

The phosphate solution will be slowly dripped into the calcium solution under vigorous magnetic stirring (350 rpm) at 50°C. The dripping rate will be controlled at 10 mL/min for 100 minutes to avoid rapid precipitation. The Ca/P molar ratio will be maintained at approximately 1.5 (the stoichiometric ratio for β-TCP, $Ca_3(PO_4)_2$, is 3:2=1.5). The resulting suspension will be aged for 24 hours at room temperature to promote crystallization and phase stabilization. The precipitate will be separated by filtration and repeatedly washed with deionized water until the filtrate reaches neutral pH, ensuring removal of residual ions and contaminants. The washed precipitate will be dried in an oven at 110°C for 3 hours, followed by recalcination at 900°C for 8 hours to ensure phase conversion to pure β-TCP and enhance crystallinity.

C. *Material Characterization*

The synthesized β-TCP will be characterized using the following techniques:

1) X-ray Diffraction (XRD):

- Purpose: To identify crystalline phases (confirm β-TCP phase), determine crystallinity degree, and detect potential impurity phases.
- Procedure: Powdered samples will be analyzed using an X-ray diffractometer with Cu-Kα radiation. Diffraction patterns will be recorded over a specific 2θ range and compared with the Joint Committee on Powder Diffraction Standards (JCPDS) database for phase identification.

2) Scanning Electron Microscopy (SEM):

- Purpose: To analyze surface morphology, particle size, and microstructure of synthesized β-TCP powder.
- Procedure: Samples will be coated with a thin conductive layer (e.g., gold) and observed under a scanning electron microscope. SEM images will be captured at various magnifications to obtain detailed surface characteristics.

III. RESULTS AND DISCUSSION

The β-TCP compound was synthesized from 2.83 g of CaO derived from Batik clam shells and 4.245 g of $(NH_4)_2HPO_4$. Figure 1 shows the XRD diffraction pattern of the characterized β-TCP.

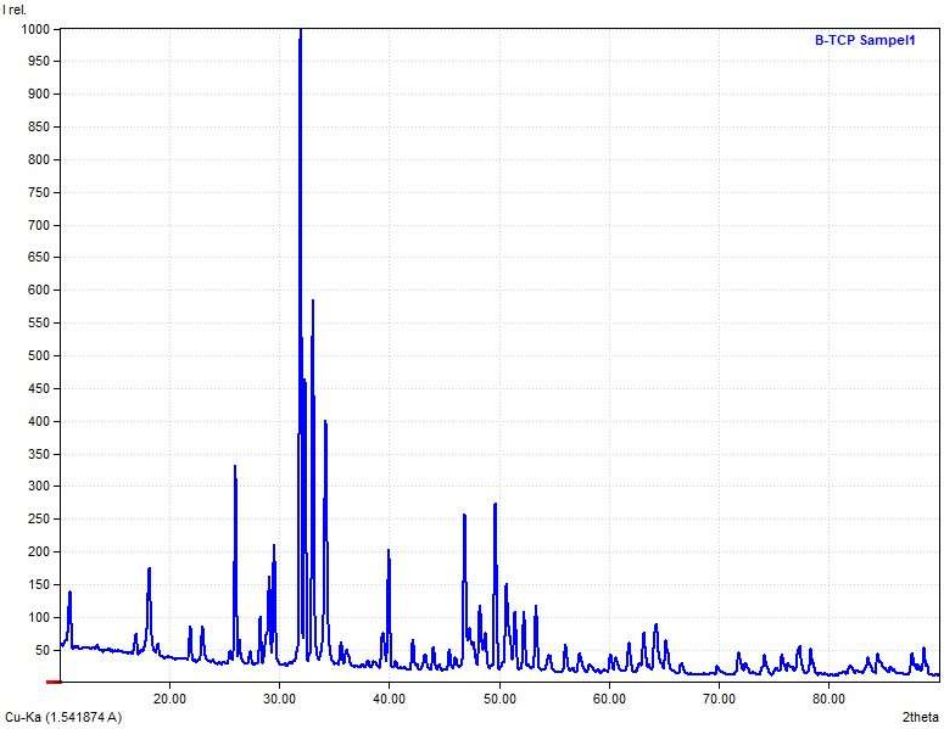

Figure 1. XRD diffraction pattern of β-TCP from Batik clam shell CaO source with 8 hours calcination

X-ray diffraction measurement and phase identification of the synthesized β-TCP (Figure 1) revealed characteristic diffraction peaks between 2θ angles of 10-65°. Phase identification was performed by comparing the diffraction pattern with β-TCP compounds in the Crystallography Open Database (COD).

The observed peaks were matched using analysis software and found to correspond well with β-TCP in the COD database (ID 1517238). The database information indicates the formed β-TCP compound has the crystalline phase with structural parameters shown in Table 1.

Table 1. Structural parameters of β-TCP compound from COD database (ID 1517238)

Chemical Name	$Ca_3 (P O_4)_2$
Formula	$Ca_3 O_8 P_2$
Calculated formula	$Ca_{2.98} O_8 P_2$
Title of publication	Crystal structure analysis of beta-tricalcium phosphate Ca3(PO4)2 by neutron powder diffraction
Authors of publication	Arnold, Emily L.; Keeble, Dean S.; Evans, J. P. O.; Greenwood, Charlene; Rogers, Keith D.
Journal of publication	Kamiyama, T.; Hoshikawa, A.; Yashima, M.; Sakai, A.
Journal of publication	Journal of Solid State Chemistry
Year of publication	2003
Journal volume	175
Pages of publication	272-277
a	10.4352 Å
b	10.4352 Å

c	37.4029 Å
α	90°
β	90°
γ	120°
Cell volume	3527.26 Å^3
Number of distinct elements	3
Hermann-Mauguin symmetry space group	R 3 c :H

The crystalline peaks of β-TCP appeared at 2θ angles of: 26.05°, 29.57°, 32.37°, 34.25°, 46.88°, 48.26°, and 53.36°. However, several high-intensity peaks not corresponding to β-TCP were observed at 2θ = 29.11°. Further peak matching identified these as β-calcium pyrophosphate (β-$Ca_2P_2O_7$), formed due to incomplete heating processes [13].

The β-$Ca_2P_2O_7$ phase is an intermediate product in β-TCP formation through the chemical reaction between $Ca(OH)_2$ and H_3PO_4:

$$2Ca(OH)_2 + 2H_3PO_4 \rightarrow 2CaHPO_4 + 4H_2O\uparrow$$

At temperatures above 520°C, $CaHPO_4$ transforms into β-$Ca_2P_2O_7$:

$$2CaHPO_4 \rightarrow \beta\text{-}Ca_2P_2O_7 + H_2O\uparrow$$

With complete heating at 700-900°C, β-$Ca_2P_2O_7$ further transforms into β-TCP by incorporating CaO:

$$\beta\text{-}Ca_2P_2O_7 + CaO \rightarrow \beta\text{-}Ca_3(PO_4)_2$$

Quantitative analysis revealed the identified β-TCP phase constituted 67.9% of the sample, while β-$Ca_2P_2O_7$ accounted for 32.1%. The crystal system of β-TCP was trigonal (hexagonal axes) with lattice parameters a = 10.43520 Å and c = 37.40290 Å, while β-$Ca_2P_2O_7$ formed a triclinic (anorthic) system with parameters a = 6.66600 Å, b = 6.72200 Å, and c = 6.73740 Å.

2. Micrograph Analysis of β-TCP Using Scanning Electron Microscopy (SEM)

Morphological analysis of β-TCP was performed using SEM, focusing on pore size identification. Figures 2-4 show SEM images at 500×, 1000×, and 5000× magnification of β-TCP samples derived from Batik clam shell $CaCO_3$ calcined at 900°C for 8 hours.

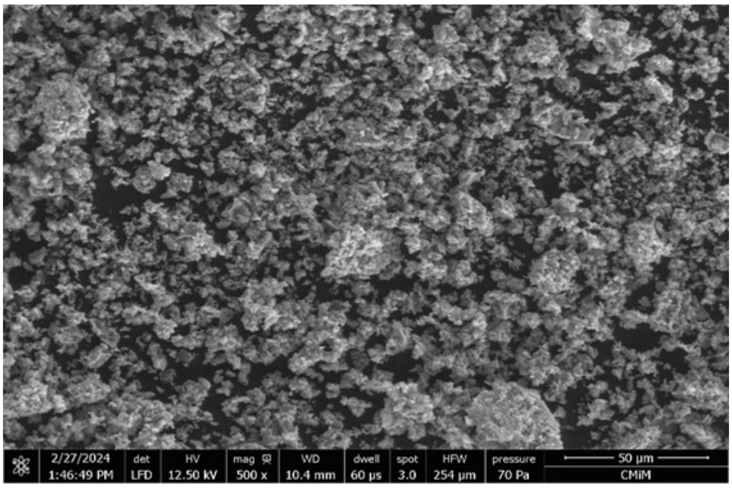

Figure 2. SEM micrograph of β-TCP sample at 500× magnification

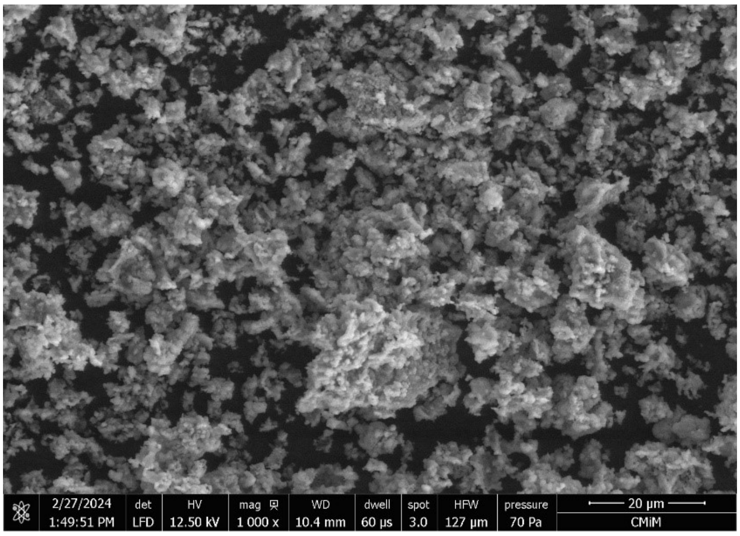

Figure 3. SEM micrograph of β-TCP sample at 1000× magnification

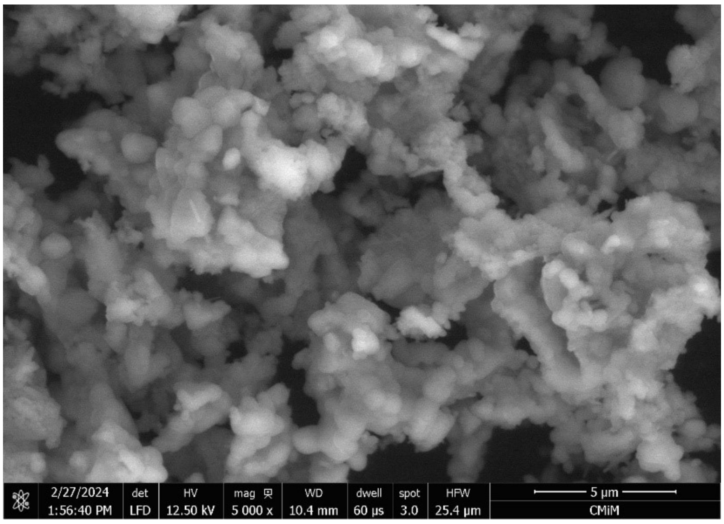

Figure 4. SEM micrograph of β-TCP sample at 5000× magnificatio

The images show particle size distributions of approximately 50 µm (500×), 20 µm (1000×), and 5 µm (5000×). The powder surface exhibited uniform particle distribution with some agglomeration. The morphology appeared irregular with particle aggregates. Higher sintering temperatures caused particle fusion, forming larger particles. The constituent particles of β-TCP ranged between 500-1500 nm [14].

IV. CONCLUSIONS

This study successfully synthesized β-Tricalcium Phosphate (β-TCP) from Batik clam shells using a precipitation method with calcination at 900°C for 8 hours. XRD characterization revealed the primary product was β-TCP (67.9 vol%), accompanied by a secondary phase of β-calcium pyrophosphate (β-$Ca_2P_2O_7$, 32.1 vol%). SEM analysis demonstrated that the synthesized β-TCP exhibited a coarse agglomerated morphology composed of particle clusters with two dominant sizes: larger chunks averaging 1.5 µm and smaller fragments averaging 0.5 µm.

REFERENCES

[1] Dorozhkin, S. V. (2007). Calcium orthophosphates. Journal of Materials Chemistry, 17(30), 3045–3067.

[2] Bohner, M. (2010). Calcium orthophosphates in medicine: from ceramics to calcium phosphate cements. Injury, 41, S8–S13.

[3] Daculsi, G. (2009). The use of absorbable calcium phosphate ceramics for bone defect filling and bone tissue engineering. Key Engineering Materials, 396–398, 23–28.

[4] Yang, S., Zhang, W., & Feng, C. (2011). Synthesis of β-tricalcium phosphate powders by wet precipitation method. Materials Letters, 65(13), 1957–1959.

[5] Raynaud, S., Champion, E., & Bernache-Assollant, D. (2002). Calcium phosphate apatites with variable Ca/P atomic ratio: Synthesis and thermal stability. Biomaterials, 23(1), 193–202.

[6] Susanti, D., & Pradana, R. A. (2018). Synthesis of β-Tricalcium Phosphate from Green Mussel Shell (Perna viridis) as Calcium Source for Bone Graft. Materials Science Forum, 931, 377–381.

[7] Lestari, D. A., & Setyarini, Y. (2019). Sintesis β-Tricalcium Phosphate dari Cangkang Kerang Ranga sebagai Kandidat Biomaterial Implan Tulang [Synthesis of β-TCP from Rangga Clam Shells as Bone Implant Biomaterial Candidates]. Jurnal Rekayasa Proses, 13(2), 101–108.

[8] Rahayu, M., Setiawan, A., & Sumardi. (2020). Synthesis and Characterization of β-Tricalcium Phosphate from Pearl Oyster Shell. IOP Conference Series: Materials Science and Engineering, 833(1), 012015.

[9] Sari, D. P., Indrati, R., & Hartati, S. (2017). Sintesis Hidroksiapatit dari Cangkang Telur Ayam dengan Metode Presipitasi [Hydroxyapatite Synthesis from Chicken Eggshells via Precipitation Method]. Jurnal Bahan Alam Terbarukan, 6(1), 1–8.

[10] Al-Noamani, Z., & Al-Marsoomi, M. M. (2019). Preparation and Characterization of Hydroxyapatite from Natural Limestone. Journal of Engineering and Applied Sciences, 14(14), 4811–4816.

[11] Ramli, M. N., Mohamed, N., & Abdullah, M. Z. (2015). Synthesis of Hydroxyapatite from Natural Coral. Journal of the Australian Ceramic Society, 51(2), 173–177.

[12] Suseno, T., Nisa, S. K., & Pratiwi, D. D. (2021). Characterization of Calcium Oxide (CaO) Derived from Paphia undulata Shell through Calcination Method. IOP Conference Series: Earth and Environmental Science, 871(1), 012038.

[13] TenHusein, K. S., & Brown, P. W. (1999). Phase evolution during the formation of α-tricalcium phosphate. Journal of the American Ceramic Society, 82(11), 2813–2818.

[14] Alrefeai, M. H., Alhamdan, E. M., Al-Saleh, S., Alqahtani, A. S., Al-Rifaiy, M. Q., Alshiddi, I. F., ... & Abduljabbar, T. (2021). Application of β-Tricalcium Phosphate in Adhesive Dentin Bonding. Polymers, 13(17), 2972.