

THE EFFECT OF pH ON THE SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE-POLYETHYLENE GLYCOL COMPOSITES BY *IN-SITU* PROCESS

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ABSTRACT

Hydroxyapatite (HAp) has a structure and chemical composition similar to bone and teeth, so HAp is widely used in the biomedical field. However, HAp has the disadvantage of being brittle, so it needs to be composited with polyethylene glycol (PEG) using an in-situ method with the aim of improving the mechanical properties of HAp. X-Rays Diffraction (XRD) results show a diffraction pattern at an angle of 2θ which is in accordance with the HAp standard (ICSD #97849). Fourier-Transform infrared (FTIR) characterization showed the presence of HAp and PEG functional group vibrations. Characterization of Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) showed that the synthesis pH can be morphological and HAp ratio. Thermogravimetric Differential Analysis Thermal Analysis (TGA-DTA) analyzed that the HAP/PEG composites decreased in weight at temperatures $>200^{\circ}\text{C}$ due to the decomposition of organic compounds originating from PEG. The results of the HAp/PEG composite degradation behavior test showed that pH 10 was the optimum synthesis pH.

Keywords: Hydroxyapatite, Composite HAp/PEG, Characterization, Polyethylene Glycol, In-Situ.

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INTRODUCTION

Anadara granosa or commonly called blood cockle shell is one type of shellfish that is economically feasible as a source of protein and minerals, blood cockle shells live by immersing themselves under the surface of the mud because shells are infauna.¹ Based on the results of XRF characterization of calcined blood cockle shells reported by Mtavangu (2022) showed the presence of CaO content of 55.95%; MgO 0.39%; Na₂O 0.83%; SiO₂ 0.65%; SO₃ 0.22%; SrO 0.1%; Fe₂O₃ 0.04%; ZrO₂ 0.02%; Al₂O₃ 0.35% and NiO 0.01%wt. The high content of calcium carbonate (CaCO₃) in blood cockle shells is widely used as a source of calcium for synthesizing hydroxyapatite with beneficial properties such as good biocompatibility so that it can be used as a bone formation biomaterial.² Hydroxyapatite is a crystalline molecule with a molecular formula of Ca₁₀(PO₄)₆(OH)₂ composed of phosphorus and calcium and has a structured molecule comprising PO₄³⁻ tetrahedra, an O-H group, and calcium. Hydroxyapatite has Ca²⁺ sites surrounded by PO₄ tetrahedra parallel to the hexagonal axis and is of great interest in many fields due to its ion exchange, adsorption, and acid-base characteristics.^{2,3} Hydroxyapatite was included mineral of apatite a bioactive ceramic material, which has a structure and chemical composition similar to bone and teeth, so hydroxyapatite is widely used in the biomedical field as a bone graft material or teeth.⁴ Hydroxyapatite is a good bioactive ceramic material used as a biomedical implant that can help the bone regeneration process because hydroxyapatite material has good biocompatibility and bioactivity properties.⁵ Chemically hydroxyapatite, similar to the composition of bone matrix, and thermodynamically stable in bodily fluid systems. These properties lead to the usage of HAp in a variety of biomedical applications, particularly in orthopedics and orthodontics for implants and coating or loading bone-bearing repair materials. However, there are significant limitations to HAp that limit its overall efficacy. Some are fragile, have poor toughness and hardness, and have a low elastic

modulus. Thus, integrating HAp with other materials as reinforcement could be a method for increasing HAp's capabilities for biomedical applications. A variety of different elements were employed to create a hybrid compound with HAp. Metals, oxides, carbon-based compounds, and polymers were among them.⁶ Hydroxyapatite can be synthesized with various sources of calcium from natural materials or biomaterials derived from shellfish, coral, egg shells, human bones, cow bones, and limestone.⁷ The in-situ method can be used to avoid severe particle agglomeration in composites obtained from mechanically obtained Hap particles into polymer solutions.^{8,5} The in-situ method has advantages over the ex-situ method in the modulus of elasticity and mechanical properties of the resulting nanocomposite. In addition, the in-situ method can be used to synthesize Hap composites because of its light conditions, low cost, ease of synthesis, and promising large-scale production.^{9,5} Polyethylene Glycol (PEG) is a polymer that can be used to form composites with hydroxyapatite, PEG can be composited with hydroxyapatite because PEG is a polymer material that has flexible, biocompatible, non-toxic, non-irritating properties, has high ductility and toughness and can form and control pure pore size and structure. With the formation of this hydroxyapatite-polyethylene glycol (Hap/PEG) composite, it is hoped that it will improve the mechanical properties of hydroxyapatite. In addition, PEG also plays an essential role because it can cover the pores of hydroxyapatite. The greater the composition of PEG composited with hydroxyapatite, the resulting composite has a high density and hardness value.¹⁰ Similar research has also been carried out previously by comparing the concentration and temperature of synthesis, but this is not enough to conclude the effectiveness of Hap-PEG composite synthesis, so it is also necessary to know the effect of pH variation treatment on Hap-PEG composites.^{11,12} Treatment of variations in pH is the main factor that affects the formation of nanoparticles, Hap particle size, morphology, and Hap crystal purity and can change the mechanical properties of the resulting bioceramics.¹³ Therefore, this study aims to synthesize and characterize by examining the effect of pH 7, 8, 9, 10, and 11 treatments on the Hap/PEG composite with the hydroxyapatite source used derived from natural ingredients, namely blood cockle shells (*Anadara granosa*).

EXPERIMENTAL

Chemicals and Instruments

The materials used in this study included blood cockle shells (*Anadara granosa*), distilled water, diammonium phosphate ((NH₄)₂HPO₄), ammonium hydroxide (NH₄OH), nitric acid solution (HNO₃) p.a, polyethylene glycol (PEG) 6000, Phosphate-Buffered Saline (PBS, pH = 7.4). The instrument used in this research is a grinder (Fritsch Pulverisette 16), glassware (pyrex), mortar, pestle, spatula, analytical scale, oven, pH indicator paper, magnetic bar, hot plate and magnetic stirrer, aluminum foil, furnace (Thermo Insight). The characterization instruments used were *X-Ray Diffraction* (XRD with PANalytical X'Pert PRO-MPD PW3040/60), *Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy* (SEM-EDS with FESEM Thermo Scientific Quattro S), *Fourier-transform infrared* (FT-IR with PerkinElmer Frontier Spectrometer) *Thermogravimetric Analysis-Differential Thermal Analysis* (TGA-DTA with Shimadzu dtg-60 & Shimadzu ta-60 instrument).

Preparation of CaO Powder from Blood Cockle Shells (*Anadara granosa*)

Clean the shells first, then grind them using a grinder until they become powder. Blood cockle shell powder was calcined for 5 hours at 900°C to obtain CaO powder.

In-Situ Synthesis of Hydroxyapatite-Polyethylene Glycol Composites

Dissolved 4 grams of Polyethylene Glycol (PEG) in 15 mL of distilled water while stirring using a stirrer. The concentration of hydroxyapatite particles was adjusted to 70 wt% by dissolving CaO powder in 50 mL of 2 M HNO₃ for 15 minutes to form a Ca(NO₃)₂ solution and then filtered. Ca(NO₃)₂ filtrate was added to the PEG solution and stirred for 20 minutes, pH was varied to 7, 8, 9, 10, and 11 by adding ammonium hydroxide (NH₄OH). In a separate beaker, the diammonium phosphate ((NH₄)₂HPO₄) was stirred in 6 mL of distilled water. This solution was added to a mixture of Ca(NO₃)₂ and PEG solution drops per drop and adjusted the pH variation of the solution was while stirring using a stirrer for 2 hours at 60°C to reach a Ca/P molar ratio of 1.67. The obtained HAp/PEG nanocomposite was transferred to a petri dish and oven for 48 hours at 70°C. Then the HAp/PEG nanocomposite powder was analyzed using FT-IR, XRD, SEM-EDS, and TGA-DTA characterization and degradation behavior test.⁵

Preparation of Phosphate-Buffered Saline Solution (PBS, pH = 7.4)

Dissolve 2.38 grams of disodium hydrogen phosphate (Na_2HPO_4), 0.19 grams of potassium dihydrogen phosphate (KH_2PO_4), and 8 grams of sodium chloride (NaCl) with distilled water until it reaches a volume of 1 L. Then the pH is measured until it comes to a pH of 7.4 by adding 0.1 M NaOH.¹⁴

Hydroxyapatite-Polyethylene Glycol Composite Degradation Behavior Test

The samples were immersed in Phosphate-Buffered Saline (PBS) with a pH of 7.4 for different periods of up to 12 days, removed, and the samples were dried at intervals of 2 days. Determine the percentage of degradation D (%) using the following equation:

$$D (\%) = (W_d/W_0) \times 100\% \quad (1)$$

W_d and W_0 are the sample weights after and before degradation, respectively.⁷

RESULTS AND DISCUSSION

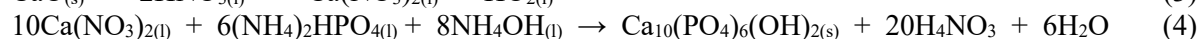
CaO Powder from Blood Cockle Shells (*Anadara granosa*)

Blood cockle shell (*Anadara granosa*) is a biomaterial with a composition of about 98% calcium carbonate. With this amount of composition, blood cockle shells can be used as a source of calcium in the synthesis of hydroxyapatite. Preparation of CaO powder from blood cockle shells was calcined at a temperature of 900°C. In which this calcination process aims to eliminate organic compounds that interfere with the HAP formation process, and calcium carbonate compounds (CaCO_3) contained in blood cockle shells can be reduced to calcium oxide (CaO).¹⁵ The reactions that occur in this calcination process are:



In-Situ HAP/PEG Composite

The addition of polyethylene glycol (PEG) in the synthesis of HAP/PEG composites can affect the crystal structure of the resulting composite. During the sintering process, the atoms making up the HAP/PEG composite undergo a phase change from amorphous to crystalline. In addition, the addition of PEG also plays an important role because it can cover the pores of hydroxyapatite.¹⁰ The reaction for the formation of hydroxyapatite that occurs:



Effect of pH in HAP/PEG Composite Synthesis

Based on Fig.-1 it can be observed that the results of the synthesis of the HAP/PEG composite with the treatment of variations in pH can affect the mass of the resulting HAP/PEG composite. In this study, the higher the pH, the more group of the HAP/PEG composite produced. This is by Palanivelu, R. A *et al.*, (2014), which showed that at a low pH, the reaction between Ca^{2+} and PO_4^{3-} was less rapid, while at a high pH the reaction between Ca^{2+} and PO_4^{3-} took place quickly to produce a larger mass of HAP/PEG composite.¹⁶

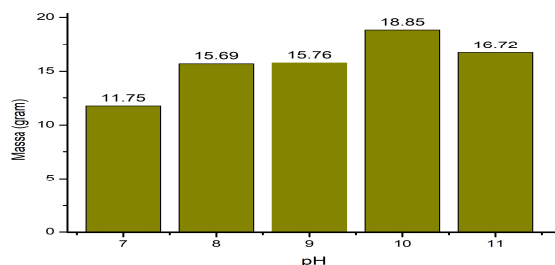


Fig.-1: Effect of pH on HAP/PEG Synthesis

Based on the results, the HAP/PEG composite mass was more abundant in the HAP/PEG composite pH 10 and pH 11. Therefore, further research was carried out to characterize the HAP/PEG composite pH 10 and pH 11 using *X-Ray Diffraction (XRD)* and *Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS)*, *Thermogravimetric Analysis-Differential Thermal Analysis (TGA-DTA)* characterization was carried out on HAP/PEG pH 10 composites. In addition, characterization was carried

out with *Fourier-transform infrared* (FT- IR) and degradation behavior test on HAp/PEG composites with variations in pH 7, 8, 9, 10, and 11.

HAp/PEG Composite XRD Analysis

X-Ray Diffraction (XRD) analysis was used to identify the crystal structure and size of the HAp/PEG composite formed from the synthesis that had been carried out by comparing the data obtained with the HAp standard (ICSD #97849). Figure-2 is an XRD diffraction, in which it can be observed that the HAp sample has a hexagonal structure that appears at peaks of $2\theta = 30.28$ and 32.38° , which corresponds to the HAp standard (ICSD #97849). The addition of PEG in HAp synthesis can affect the crystal structure of HAp which is characterized by the appearance of a new peak detected at $2\theta = 23.40^\circ$, the highest peak in the sample.¹⁰

In XRD analysis, the crystal size of the resulting sample is determined through *Scherer* calculations with the *Deybe Scharer* equation as follows:

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (5)$$

L = crystal size (nm); k = constant (0.9); λ = X-ray wavelength; β = FWHM (Full Width at Half Maximum) at 2θ (π 180); θ_B = Bragg angle.

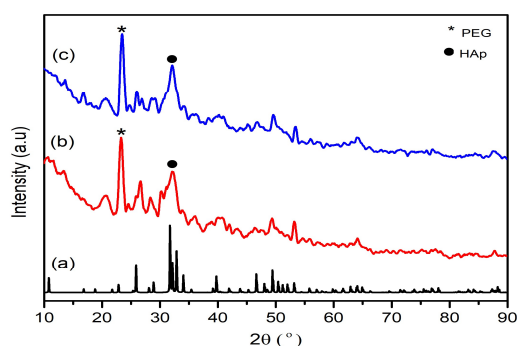


Fig.-2: XRD Pattern (a) Pure HAp (b) HAp/PEG Composite pH 10 and (c) pH 11

Based on Table-1, it can be observed the crystal size of HAp, where the pH variation treatment affects the crystal size of HAp. The smaller HAp crystal size has better bioactive properties and can form new tissue growth faster in the body.^{17,18} From the measurement results using the *Scherer* equation, the crystal size of HAp in the HAp/PEG composite synthesized at pH 10 and pH 11 was 52.92 nm and 53.15 nm, respectively, these results indicate the crystal size of HAp in the synthesized HAp/PEG composite. At pH 10 and pH 11 correspond to the crystal size of human bone HAp around 20-80 nm.¹⁰

Table-1: HAp Crystal Size in HAp/PEG Composites

Sample	Peak 2θ (deg)	FWHM (deg)	Crystal Size (nm)
HAp/PEG pH 10	30.02	0.16	52.92
HAp/PEG pH 11	31.75	0.16	53.15

FTIR Analysis of HAp/PEG Composites

HAp/PEG composites were analyzed by *Fourier-transform infrared* (FT-IR) to identify functional groups in the form of absorption peaks contained in hydroxyapatite-polyethylene glycol composites, in which FT-IR analysis was carried out at a wave number of $4000-400\text{ cm}^{-1}$. Based on the results of the FTIR spectrum data for the synthesis of HAp/PEG composites in Fig.-2.(a-e), it can be observed that there are typical peaks of HAp, namely the peaks of the PO_4^{3-} and O-H groups.¹⁹ While the results in Fig.-3.(f), which is the FT-IR spectrum of pure PEG, show the presence of peaks in the vibrations of the O-H, C-H, C-C, -C-O-C- bonds and the H-C-H bonds, which are the constituent bonds of the PEG polymer.²⁰ The peak of the OH-group is found at wave number 3185.24 cm^{-1} . At the wave number $540-555\text{ cm}^{-1}$, there is vibrational bending, and asymmetric stretching at the wave number $1020-1040\text{ cm}^{-1}$ from PO_4^{3-} .^{21,22} While at 904 cm^{-1} , the wave number of the PO_4^{3-} the group is symmetric vibrational stretching.²³ From the FTIR spectrum, it has shown the presence of apatite compounds which PO_4^{3-} characterizes peaks, the presence of PO_4^{3-} and

O-H groups which are functional groups of HAp, indicating the presence of HAp content in the sample.^{15,16} In addition, at wave numbers 1430 cm^{-1} and 2897.66 cm^{-1} , respectively, it is caused by the bending vibration of the C-H bond and the stretching of the C-H bond vibration originating from PEG. This results are consistent with the results of our previous research with differences in temperature and concentration of synthesis.^{11,12,20}

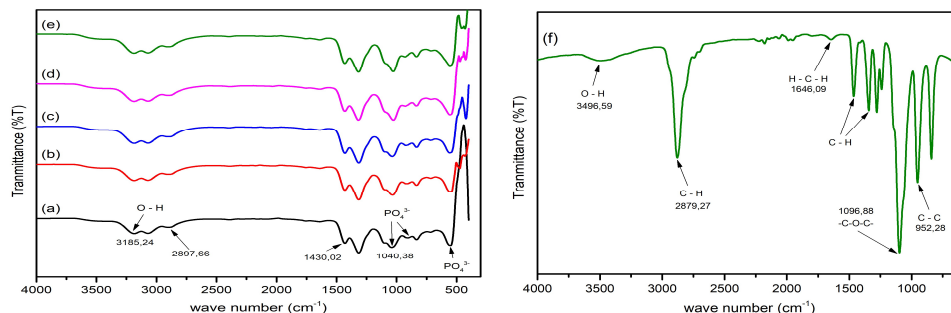


Fig.-3: FT-IR Spectrum of HAp/PEG Composite with Variations of (a) pH 7, (b) pH 8, (c) pH 9, (d) pH 10, (e) pH 11 and (f) Pure FT-IR PEG Spectrum

SEM-EDS Analysis of HAp/PEG Composites

Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) analysis was used to determine the surface morphology and the elemental content in the HAp/PEG composite with a magnification of 10,000x, 20,000x, 30,000x, and 40,000x.¹⁵ Figures-4 and 5 are SEM analyses of the HAp/PEG composite pH 10 and pH 11 with almost the same size and morphology, showing a needle-like aggregate structure characteristic of HAp particles, this is slightly different from the result of our previous research with different temperatures, where the results had two particle characteristics. The result of particle size analysis of the HAp-PEG composite pH 10 was 5.1 while at pH 11 was 6.5 nm, this indicates that pH affects particle size. In addition, the SEM analysis also observed that the sample showed agglomeration. In the HAp/PEG pH 11 composite sample, more agglomeration was formed than in the HAp/PEG pH 10 composite. This was due to the higher pH in the HAp/PEG composite synthesis causes the reaction between Ca^{2+} and PO_4^{3-} to occur faster, so that agglomeration in the composite sample is formed faster.¹⁶

Table-2: Elemental Content in HAp/PEG Composite and Ca/P Molar Ratio

pH	Elemental Content (wt %)				Ca/P Molar Ratio
	Ca	P	C	O	
10	8.61	4.58	49.25	37.56	1.87
11	13.13	6.55	43.16	37.16	2.00

From the data in Table-2. the results of the measurement of the Ca/P molar ratio that deviates from the stoichiometric Ca/P molar ratio value of 1.67 in the HAp/PEG composite are 1.87 and 2.00, indicates that the treatment of pH variations can affect the value of the Ca/P molar ratio. The higher the pH used for synthesizing the HAp/PEG composite, the resulting Ca/P molar ratio value also increases. This occurs because the interaction between Ca^{2+} and PO_4^{3-} is high at high pH so that it can produce a Ca/P molar ratio value which tends to increase. However, the Ca/P molar ratio produced by the HAp/PEG composite sample at pH 10 of 1.87 and pH 11 of 2.00 is still included in the range of HAp formation.¹⁶

TGA-DTA Analysis of HAp/PEG Composites

Thermogravimetric Analysis-Differential Thermal Analysis (TGA-DTA) was used to determine the weight loss of the HAp/PEG composite sample, which was carried out at a temperature range of 0°C to 900°C . In Fig.-6 the temperature region less than 200°C shows the first weight loss in the sample caused by the adsorbed water molecules and the removal of lattice water in the HAp/PEG sample. Meanwhile, in the temperature region $> 200^\circ\text{C}$, the second and third weight loss occurred in the HAp/PEG composite sample caused by PEG degradation and the dehydration reaction of the C-OH group from the PEG chain.^{23,24}

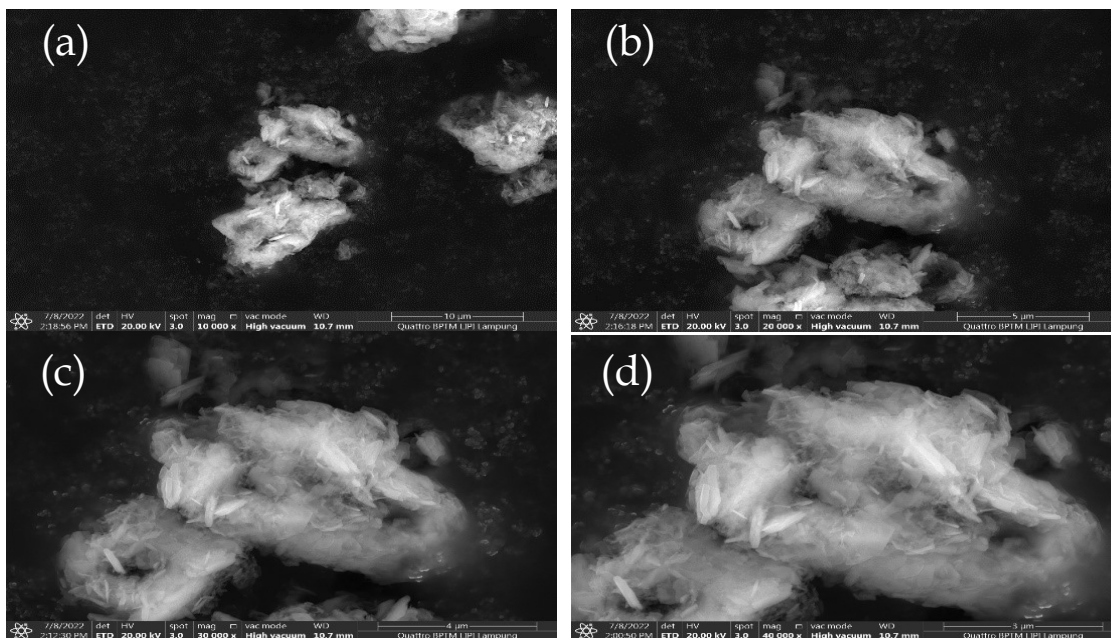


Fig-4: SEM Morphology of HAp/PEG Composite pH 10 Magnification (a) 10,000x, (b) 20,000x, (c) 30,000x, and (d) 40,000x

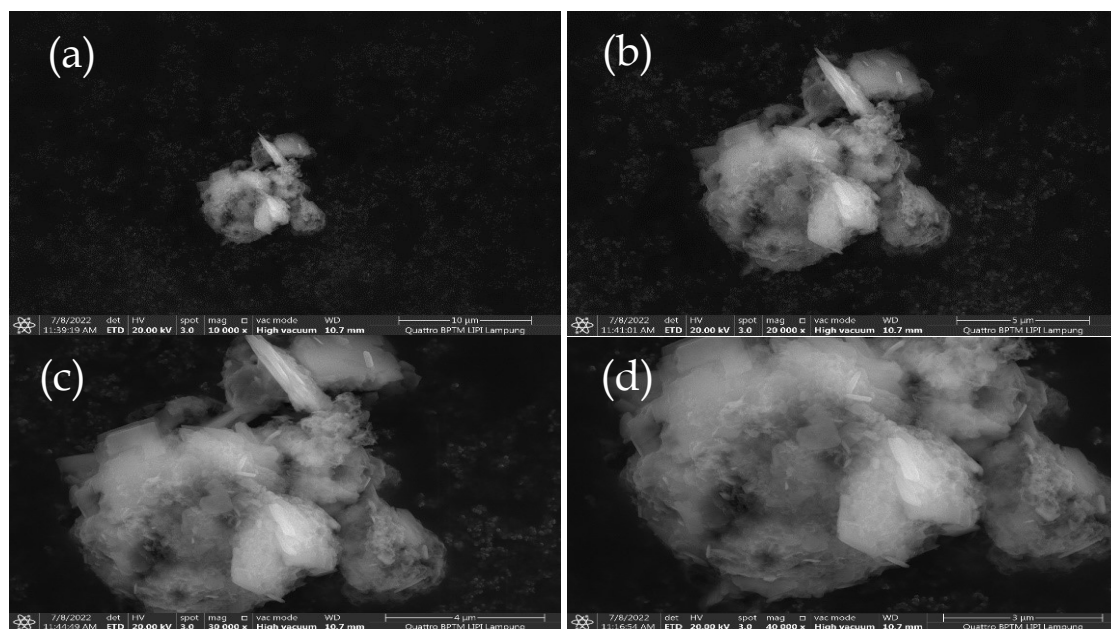


Fig-5: SEM Morphology of HAp/PEG Composite pH 11 Magnification (a) 10,000x, (b) 20,000x, (c) 30,000x, and (d) 40,000x

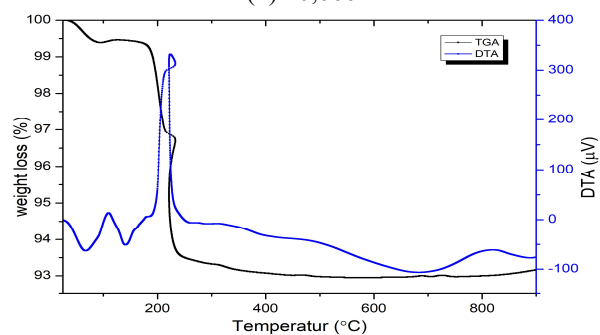


Fig-6: Graph of TGA-DTA Composite HAp/PEG at pH 10

HAp/PEG Composite Degradation Behavior Test

The degradation behavior test on composites was conducted to determine the biodegradation properties of HAp/PEG composites as bone implants. The degradation test was carried out on samples of HAp and HAp/PEG composites with variations in pH 7, 8, 9, 10 and 11 by immersing the sample in a solution of Phosphate-Buffered Saline (PBS, pH = 7.4). Based on Fig.-7. shows pure PEG and HAp/PEG composite can be degraded. On the 2nd day to the 12th day of immersion PEG was degraded entirely in PBS solution. This happened because PEG is a flexible polymer that can dissolve in water, methanol, benzene and dichloromethane, which can be used for the synthesis of Hap.²⁵ In addition, it can also be observed in Figure 6. showing the lower the pH, the more easily degraded the HAp/PEG composite sample, which is indicated by a decrease in the weight of the composite sample as the sample is immersed in PBS solution. The immersion of the HAp/PEG composite, which was synthesized at low pH with PBS solution, resulted in a powdered sample. This happened because at low pH, it had poor hardness due to the lack of reaction between Ca^{2+} and PO_4^{3-} thus allowing the sample to be quickly degraded.¹⁶ In bone implants, the rate of degradation must be by bone growth, and if the rate of degradation is high, it can decrease the mechanical properties of the sample and result in the failure of bone implants, as well as at a lower rate of degradation, it will result in incomplete bone growth failing bone implants.²⁶ Therefore, the rate of degradation of the sample needs to be considered.

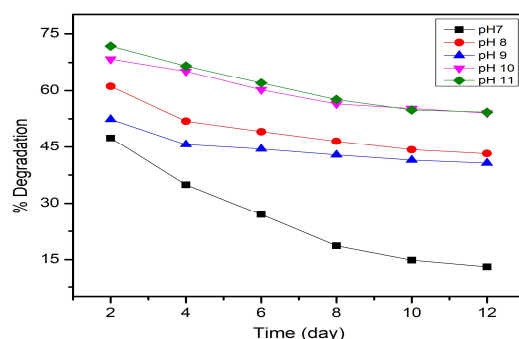


Fig.-7: Graph of % Degradation of Pure PEG and HAp/PEG Composites at Various pH 7, 8, 9, 10, and 11

CONCLUSION

Based on the research that has been done, it can be concluded that the HAp/PEG composite was successfully synthesized *in-situ* with blood cockle shells (*Anadara granosa*) and showed that there was an effect of pH variation on crystal size, morphology, mass-produced and the rate of degradation of the HAp/PEG composite. The XRD results show that the sample has a larger crystal size as the pH increases. The SEM-EDS results show that the HAp/PEG composite pH 10 and pH 11 form a needle-like structure and produce a higher Ca/P molar ratio that increases with increasing pH. From the results degradation test, the lower the pH, the faster the rate of degradation of the HAp/PEG composite with the duration of immersion of the sample in PBS solution. So it can be concluded that pH 10 is the best in this study because it has good bioactive properties and produces more HAp/PEG composites.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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