

# Coating hydroxyapatite on stainless steel 316 L by using sago starch as binder with dip-coating method

**A Fadli , F Akbar, A Prabowo and P H Hidayah**

Chemical Engineering Department, Faculty of Engineering, University of Riau

E-mail : fadliunri@yahoo.com

**Abstract:** Hydroxyapatite (HA) is a mineral form of naturally occurring apatite calcium with  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  formula. One of the major innovations in the field of bone reconstruction is to apply HA as a surface coating on a mechanically strong implant metal and to improve the stability of bone implants thereby increasing the lifetime of the metal implants. Pure hydroxyapatite has poor mechanical properties so it is necessary to add sago starch as a binder to combine the strength and hardness of metal surfaces with bioactive properties of hydroxyapatite by Dip Coating method. Stainless steel 316L is the most commonly used alloy as an implant for bones and teeth due to its excellent corrosion and oxidation resistance and is easily formed. In this study, hydroxyapatite coatings used fixed variables as hydroxyapatite mass (10 grams), aquades mass (20 grams), dipping time (20 seconds), and calcination conditions (800°C, 1 hour). The variables are sago starch mass (1, 1.25, 1.5 gram) and stirring time (16, 20, 24 hours). The shear strength value is higher in the addition of 1.25, 10, 20, and again in the binder ratio of 1.5; 10; 20. The addition of stirring time causes a decrease in shear strength. The highest shear strength value obtained was 3.07 MPa. The layer attached to the substrate is a hydroxyapatite with a composition of 99.4% as evidenced by the results of XRD analysis.

## 1. Introduction

The number of accidentsemerge either light or heavy is relatively hugein every year. One of the most common cases of accidents are the fractures. This case can also occur due to osteoporosis. The high of fractures causes the high demand for bone implants. Hydroxyapatite has been known to be a good substitute for bone and dental implants in the health world due to its chemical and biological resemblance to human bone tissue. Stainless steel 316L is one of the most commonly used materials for implant. Stainless steel resistance to corrosion is one factor of stainless steel selection as bone and dental implants. In addition stainless steel has an affordable price compared to other metals such as titanium, so that affordable implants can be obtained using stainless steel as an implant[1]. One of the factors affecting the strength of adhesion on the hydroxyapatite coating is the binder, in which the binder serves to assist the deposition process that occurs on the surface of the substrate. Sago is a tropical plant that grows in Indonesia. Utilization of sago in the form of starch has been limited only as food. Sago can be used as a binder, thickener, and stabilizer. So in this study sago used as a binder in the process of hydroxyapatite coating on stainless steel 316L[2].The preparation of hydroxyapatite coatings can be done by various deposition methods such as thermal spraying, sputtering, EPD, and dip coating. Dip-coating method is a deposition method that has many advantages, such as low cost and simple process [3]. In addition, this method can also be used to coat the substrate with a complex form. Based on these



advantages, the dip-coating method is chosen as a deposition method in hydroxyapatite coating on stainless steel 316L.

## 2. Method

The material used in this study were hydroxyapatite, Stainless steel 316L, Acetone and Aquadest. The main tool used in this research are the dip coating unit which serves as a hydroxyapatite coating device on the substrate. In addition, the tool used in this research is furnace (Nabertherm, Germany) which serves for sintering samples, stopwatch to measure the duration of dyeing, as well as sandpaper, glass chemical, scales, and magnetic stirrer used for the preparation of suspension and substrate. Preparation of a suspension solution hydroxyapatite is weighed as much as 10 grams and fed into beaker. Then added aquades as much as 20 grams, and sago that has been weighed as much as 1; 1.25 and 1.5 grams. The solution was stirred with a magnetic stirrer for 16, 20 and 24 hours. After that preparation of the substrate, stainless steel 316L cut with size 2x3 cm, then sanded by sandpaper. Stainless steel has been sterilized by soaking in acetone for 15 minutes, after it is rinsed using aquades. The substrate is then dried using an oven at 80°C for 10 minutes. Finally, the coating process, the sterilized substrate is immersed in the suspension for 20 second, and 1 dyeing. the hydroxyapatite coated substrate was then dried at 110 °C for 30 min, then sintered at 800 °C 1h.

## 3. Result and discussion

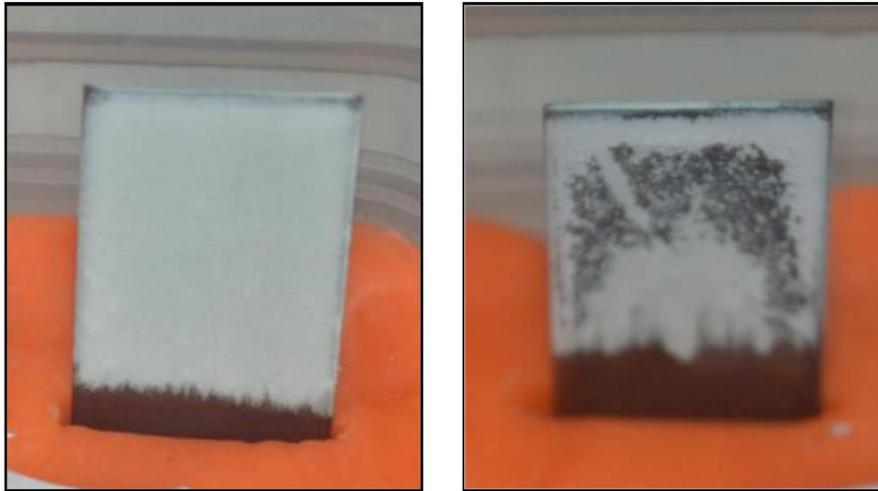
### 3.1 Result on visually analysis

Based on the results of the research, visual observations were made coatings are generated on a variety of binder and time ratios stirring. Observations were made on the deposited layer on substrate. The observations is shown in Table 1.

**Table 1.** Observations visually

Sample Code	Stirring Time	Sago Ratio: HA: Affected	Results
S1	16 Hours	1.0: 10: 20	<input type="checkbox"/> Layer Repositioned evenly
S2	16 Hours	1.25: 10: 20	<input type="checkbox"/> Nocracking <input type="checkbox"/> Layer Repositioned evenly
S3	16 Hours	1.5: 10: 20	<input type="checkbox"/> Nocracking <input type="checkbox"/> Layer uneven
S4	20 Hours	1.0: 10: 20	<input type="checkbox"/> Cracking on deposition layer <input type="checkbox"/> Layer Repositioned evenly
S5	20 Hours	1.25: 10: 20	<input type="checkbox"/> No cracking <input type="checkbox"/> Layer Repositioned evenly
S6	20 Hours	1.5: 10: 20	<input type="checkbox"/> No cracking <input type="checkbox"/> Cracking on deposition layer
S7	24 hours	1.0: 10: 20	<input type="checkbox"/> Layer Repositioned evenly
S8	24 hours	1.25: 10: 20	<input type="checkbox"/> No cracking <input type="checkbox"/> Layer Repositioned evenly
S9	24 hours	1.5: 10: 20	<input type="checkbox"/> No cracking <input type="checkbox"/> Layer Repositioned evenly

Table 1 shown that almost all samples have a uniform layer and no cracking occurs. However, in the sample using a binder ratio of 1.5: 10: 20 with a stirring time of 16 hours (S3) and 20 hours (S6) layers are unevenly deposition. This is due to the high binder ratio, so most of the deposition layers are burned out during sintering.



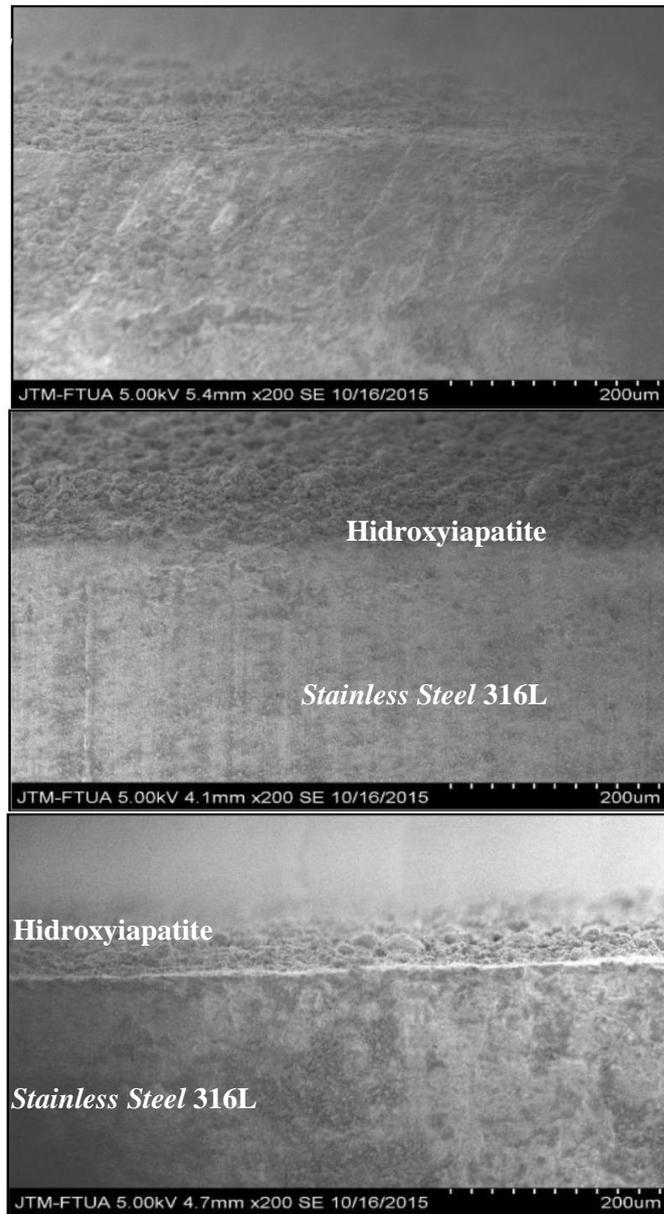
**Figure 1.** Display surface samples (a) sample (S9) and (b) sample (S3).

Figure 1 (a) displays the sample with a uniform layer and is deposited on the entire surface of the substrate. Figure 1 (b) shows samples with uneven layers. This occurs because of cracking on the surface of the coating, thus causing the deposition layer to loose from the surface of the substrate and producing coatings with uneven layers

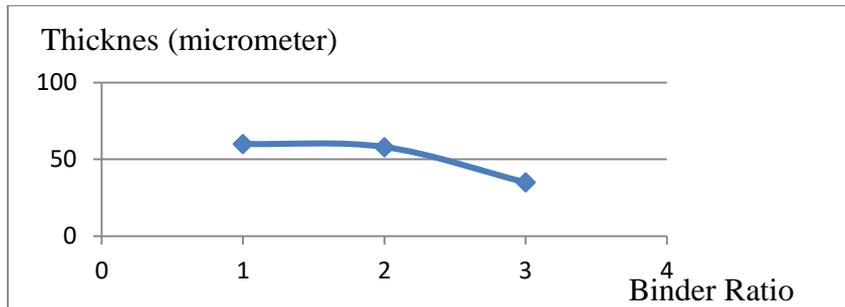
### 3.2 SEM analysis

#### 3.2.1 Effect of binder ratio against hydroxyapatite coating

The binder ratio (sago) used in the manufacture of suspensions can affect the thickness or surface state of the deposited hydroxyapatite layer. Figure 3.2 is a cross-sectional view of stainless steel 316L which has been deposited by hydroxyapatite with 24 hours stirring time at various variations of binder ratio. Base on Figure 3.2, it shown that we can measure the thickness of the hydroxyapatite layer deposited on the surface of the substrate. In the binder ratio: HA: Aquadest 1:10:20 obtained layer with a thickness of 60  $\mu\text{m}$ , while for the ratio of 1.25: 10: 20 and 1.5: 10: 20 obtained thickness of 58 and 35  $\mu\text{m}$ . Hydroxyapatite coatings to be applied as implants should have a layer thickness of 50-200  $\mu\text{m}$ , so that the coating is not lost when implanted and it still has good bond strength [4]. So the coating with the parameters is the coating produced in the ratio of 1:10:20 binder and 1.25: 10: 20 which is about 60  $\mu\text{m}$  and 58  $\mu\text{m}$ . While the binder ratio of 1.5: 10: 20 the resulting thickness is only about 35  $\mu\text{m}$ . The binder used in this study is sago starch consisting of amylose and amylopectin. Amylose is a water soluble linear chain polymer, while amylopectin is a water-insoluble polymer. Amylose and amylopectin have a hydroxyl group (-OH) that will bind to the  $\text{Ca}^{2+}$  group on hydroxyapatite. In addition, amylopectin which is a branched polymer will form a network of polymers or matrices, and the hydroxyapatite particles will diffuse into the matrix with the help of stirring.

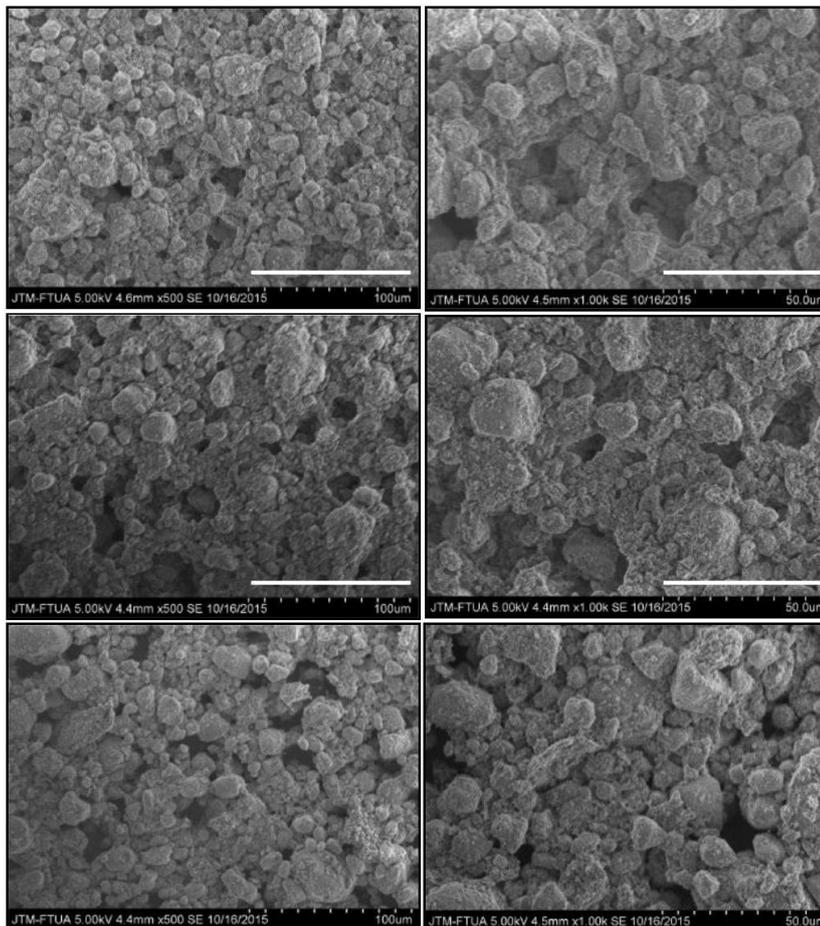


**Figure 2.** Visible stainless steel 316L strips with 24 hour stirring time and binder ratio: (a)1:10:10; (b) 1.25: 10: 20; (c) 1.5: 10: 20.



**Figure 3.** Graph of relation between coating thickness and binder ratio.

Figure 3 illustrates the relationship between the thickness of the coating and the mass of the binder. It can be seen that the resulting coating thickness decreases in the mass of the larger binder. The decrease of thickness due to the missing binder during the sintering process. The larger ratio of the binder, more hydroxyapatite particles bind to the sago starch, so the layers can run out during sintering will also increase. The layer obtained will be more thin with more binder used.



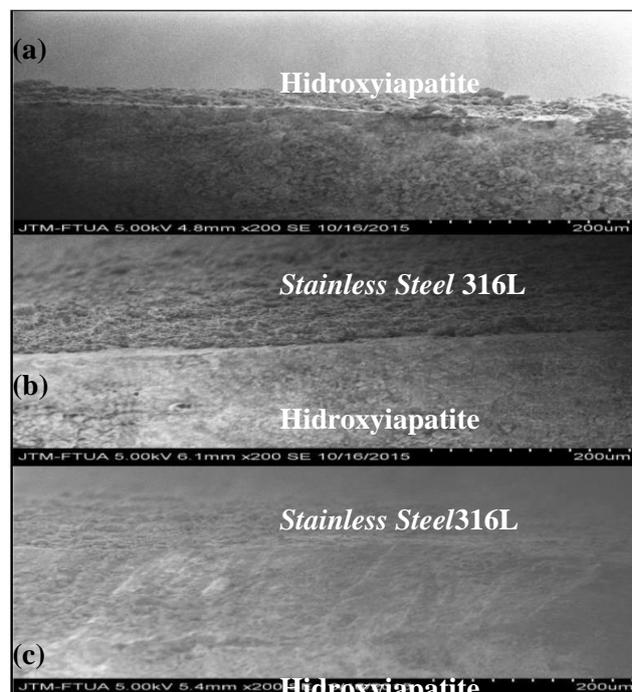
**Figure 4.** The hydroxyapatite surfaces repositioned with 24 hour stirring time and ratio: (a) and (b) 1:10:20; (c) and (d) 1.25: 10: 20; (e) and (f) 1.5: 10: 20 with magnification 500 and 1000 times.

The binder ratio in the suspension not only affected to the thickness of the resulting layer, but it also affected to the surface state of the layer. Figure 4 shown the the surface state of the deposited layer on a variety of binder ratios. Figure 4 (a) and (b) are coatings produced in a 1:10:20 binder ratio, it can be seen that there are some cavities on the surface of the layer. The cavity is more visible in larger binder ratios (Figure 4 (c) and (d)) and at the binder ratio of 1.5: 10: 20 (Figure 4 (e) and (f)) the cavity is seen more. The cavity on the surface of the coating is the result of a burning binder leaving. It can be seen that hydroxyapatite coats the entire surface of the substrate in the absence of cracking. Based on the results described previously, it can be seen that the binder ratio in the suspension is very influential on the coating produced, both thickness and surface conditions. The addition of the binder ratio in the suspension is inversely proportional to the thickness of the resulting layer, the larger the binder ratio used, the obtained layer will be thinner. In addition, the addition of the binder ratio can also cause more cavities to form on the surface of the layer.

### 3.2.2 Effect of stirring time on hydroxyapatite coatings

The hydroxyapatite coating process uses a dip coating method is performed by dipping the substrate into the suspension, where the physical properties of the suspension are one of the factors that may affected to the deposited layer. In this study coating with various stirring variations time to determine the effect on the thickness and surface conditions of the resulting hydroxyapatite coating. Figure 5 is a cross-sectional view of 316L stainless steel having been coated with hydroxyapatite using a binder: HA: aquadest ratio of 1,25: 10: 20 at various stirring times, ie 16 hours, 20 hours and 24 hours.

Based on follow Figure 3.5 it is known that at the time of stirring 16 hours obtained a layer with a thickness of about 35  $\mu\text{m}$  (Figure 5 (a)), and increased to 77  $\mu\text{m}$  at 20 hours of stirring time (Figure 5 (b)). However, the thickness of the back layer decreased at 24 hours agitation time around 60  $\mu\text{m}$  (Figure 5 (c)). From these results it is known that based on the coating thickness of the coating that qualifies as an implant is the coating obtained at the time of stirring 20 and 24 hours.



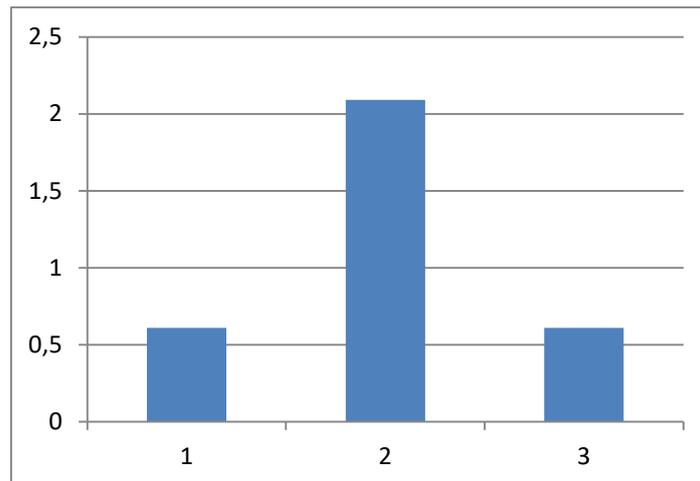
**Figure 5.** Transverse stainless steel looks repositioned with ratio binder 1:10:20 and stirring time, (a) 16 Hours, (b) 20 hours, (c) 24 hours.

### 3.3 Autograph analysis

Analysis using autograph is done to measure the strength value of the coating deposited on the surface of stainless steel. The shear strength of a layer shows how strong the layer is attached to its substrate.

#### 3.3.1 Effect of binder ratio against hydroxyapatite Coating

The strength analysis is performed on the coatings produced at 24-hour stirring time with various variations of binder ratio. The graph of the relationship between shear strength and binder ratio can be seen in Figure 6.

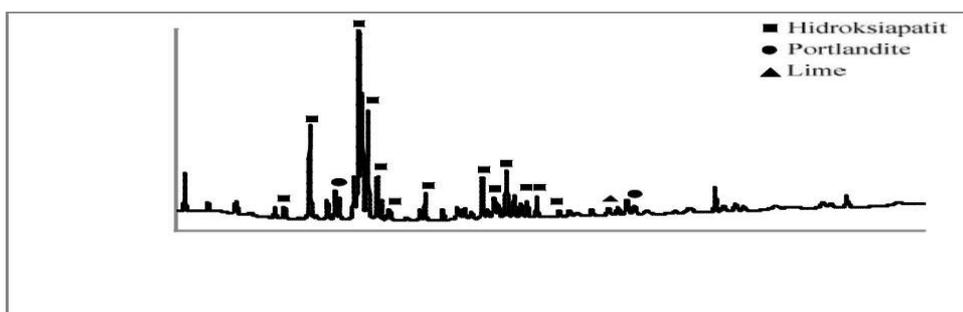


**Figure 6.** Graph relationships between shear strength and binder ratios used.

Based on Figure 6 can be seen that the ratio of 1:10:20 binder obtained shear strength value of 0.61 MPa, then at the ratio of 1.25: 10: 20 there was an increase in shear strength to 2.09 MPa, but at the ratio of 1, 5:10:20 shear strength value back down to 0.61 MPa. The addition of the binder ratio can increase bond strength to a certain point where the addition of the binder will cause a decrease in bond strength. This can happen because the bond strength is strongly influenced by the degree of homogeneity of the formed layer, the more homogeneous the layer is formed the bonding strength gets stronger [5]. In this study, the highest shear strength was obtained in the 1.25: 10: 20 binder ratio.

### 3.4 XRD analysis

XRD analysis is done to know the chemical compound in the sample and its composition. The results of the hydroxyapatite coating diffractogram with 24 hours stirring time and the 1.25: 10: 20 binder ratio can be seen in Figure 7.



**Figure 7** Diffractogram of hydroxyapatite coating results on stirring time 24 hours and binder ratio 1.25: 10: 20.

Figure 7 is a diffractogram of the resulting coating. The hydroxyapatite peaks in the image have a hkl similar to the standard hydroxyapatite characterization pattern from JCPDS (002), 112 and 300 data with angle  $2\theta$  25.879°; 32,196° and 32,902°. The peak HA contained in Figure 7 with an angle of  $2\theta$  is 25.927°; 32.262° and 32.988°. From the results of the diffractogram can also be known composition of compounds making up hydroxyapatite coating, which can be seen in Table 2.

**Table 2.** Composition of compounds available in hydroxyapatite coatings

Component	Composition (%)
Hydroxyapatite	99,4
<i>Portlandite</i> (CaOH <sub>2</sub> )	0,5
<i>Lime</i> (CaO)	0,1

Based on the results of XRD analysis it can be concluded that this hydroxyapatite coating is qualified as an implant. The minimum permissible hydroxyapatite purity was > 95% [4]. and in this study the composition of the deposited hydroxyapatite was 99.4%

#### 4. Conclusions

Hydroxyapatite coating on 316L stainless steel with sago starch binder has been successfully done by using dip coating method. The addition of stirring time causes a decrease in shear strength. The highest shear strength in this study was obtained at 16 hours of stirring time with a ratio of 1.25: 10: 20, ie 3.07 MPa.

#### References

- [1] Hermawan H, Ramdan D, and Djuansyah J R P 2011. *Metals for Biomedical Applications*, <http://www.intechopen.com/books/biomedical-engineering-from-theory-toapplications>. Accessed 26 February 2017
- [2] Belitz H D, Grosch W, and Schieberle P 2009 *Food Chemistry* 4<sup>th</sup> ed. (Berlin Heidelberg: Springer-Verlag)
- [3] Yusoff M F M, Kadir M R A, Iqbal N, Hassan M A, and Hussain R Dipcoating of poly (ε-caprolactone)/hydroxyapatite composite coating on Ti6Al4V for enhanced corrosion protection *Surf. Coat. Technol.* **245** 102-107
- [4] Heimann R B 2002 Materials science of crystalline bioceramics: A review of basic properties and applications *Chiang Mai University J.* **1** (1) 23-46
- [5] Tian T, Jiang D, Zhang J, and Lin Q 2007 Aqueous tape casting process for hydroxyapatite *J Eur. Ceram. Soc.* **27** 2671-2677