Adhesion Strength of Hydroxyapatite Coating on Titanium Alloy (Ti-6Al-4V ELI) for Biomedical Application

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Abstract. Implantation using titanium Ti-6Al-4V ELI still has disadvantages, in particular, low osseointegration cause of less bioactive of the material. Hydroxyapatite was then applied as a coating material to increase the bioactivity and the osseointegration as well. The Ti-6Al-4V ELI samples were coated with the hydroxyapatite using the electrophoretic deposition (EPD) method, with voltage variations of 5, 8 and 11 volts for 5 minutes and variations in deposition time for 5,8 and 11 minutes with voltage of 8 volt. Surface properties (coarseness, coating mass, thickness, and surface coverage) were then determined by using related equipments. Adhesion strength the HA layer was tested a cross-cut test method. The results showed that the EPD could be used properly to coat the Ti-6Al-4V ELI material with hydroxyapatite. Voltage and deposition time influence coating layer properties that is related to adhesion bonding of the layer on the metal surface. Applying the voltage of 8 volt for 5 minutes resulted in optimal surface properties with coating roughness of hydroxyapatite layer (Ra) as much as 0.88. The removed area after the cross-cut tape test is 2.25%, which means adhesion strength between the coating layer and the substrate is high enough. A relatively high hydroxyapatite mass (0.3 mg), is covering the material surface with a surface coverage of 82.1%, and the average coating thickness is 73.3 μm. Such kind of coating layer characteristics could improve bioactivity, biocompatibility and thus enhancing osseointegration capacity of prosthetic medical implants.

Keywords: hydroxyapatite, coating, titanium, bioactivity, biocompatibility

1. Introduction
Titanium α + β type Ti-6Al-4V ELI, has been used in orthopaedic applications because it has biocompatibility and relatively low modulus of elasticity [1] which can reduce the effects of stress shielding when implantation [2]. The titanium also has excellent physical and mechanical properties such as tensile and fatigue strength, low density and good corrosion resistance; those are the advantages of titanium as an implant material [3,4]. Moreover, implantation of titanium material results in a low inflammatory, hypersensitivity and allergic response when in contact with the biological environment [5].

However, titanium is bioinert or less bioactive biomaterial that produces less integration between the material with bone tissue, and it can trigger implantation failure during application in human body [6]. Titanium alloys can also corrode and even cause toxic effects on the body. Therefore, the degradation of material particles must be hindered by conducting surface modification by utilizing hydroxyapatite
(Ca_{10}(PO_{4})_{6}(OH)_{2}) which has a chemical structure similar to the bone components [7] and bioactive [8,9]. Such coating can initiate osseointegration and involved in the molecular biological mechanism of the body and accelerating the healing process of bone damage during implantation [10]. However, coating with hydroxyapatite still shows the disadvantage that there is a particle releasing due to the low bonding of coating layer to titanium substrate [5], [11]. Bond strength of coating includes adhesion strength (coating with substrate) and cohesion strength (between the hydroxyapatite particles) [12]. Furthermore, delamination and disintegration of the coatings can disrupt fixation of material to bone tissue which also trigger implantation failure [13]. Thus, the adhesion strength between hydroxyapatite layer and substrate should be high enough. The way to improve the layer adhesion can be done by the heating process. However, high temperatures result in phase transformations tend to reduce the physical properties of the coating. Hydroxyapatite coating can be carried out using the electrophoretic deposition (EPD) as an alternative method due to the efficiency of the coating process, which utilizes electric current and can be applied at low temperatures [14]. The characteristics of the coating can be controlled by treating the voltage or deposition time of the EPD coating process and followed by sintering to improve the coating adhesion. This study was conducted to determine the effect of hydroxyapatite coating by EPD method to the adhesion strength of coating layer to the Ti-6Al-4V ELI surface.

2. Materials and Methods
The Ti-6Al-4V ELI material with a size of 10mm x 4mm was used as a substrate of the study. The material was then heat-treated to reduce residual stress effect after sample preparation and also to improve the mechanical properties of the material. Solution treatment was conducted at temperature 950°C for 1 hour with a heating rate of 10°C/minute using a vacuum furnace (High-Temperature Vacuum Tube Furnace GSL-1100). The rough surface of the material was reduced by grinding process using sandpaper with mesh sizes of #120, #500, and #800. The sample was then cleaned by soaking it using ethanol solution for 15 minutes and acetone for 15 minutes in an ultrasonic bath. The sample was then immersed in the nitric acid solution for 30 minutes and NaOH solution for 1 hour and finally dried at 50°C for about 5 minutes.

Hydroxyapatite (Sigma Aldrich) with a particle size of 10μm was dissolved in ethanol (4gram/100mL). The suspension was homogenized with a stirring hot plate for 1 hour. Subsequently, nitric acid was added to reduce pH up to 4. The electrophoretic deposition was applied with the materials acts as the cathode and carbon as the anode with a distance of 1cm. The coating process was carried out by utilizing a DC digital power supply with voltage variations of 5, 8, and 11 volts for 5 minutes, and also variations in deposition time for 5,8, and 11 minutes with voltage of 8 volt. The coated material was dried for 24 hours at room temperature and then heated at 800°C for 10 minutes with a heating rate of 10°C/minute using a vacuum furnace. Microstructure observations were conducted using an optical microscope (Olympus LG-PS2). Thickness measurements were made using the Sanfix thickness gauge series GF-280, and surface roughness measurements were carried out with a surface roughness tester. The strength of the coating adhesion on the surface of the material was determined by a cross-cut tape test method based on ASTM D3359 standard.

3. Results and Discussion
Hydroxyapatite coating layer, in general, has been formed on the surface of all titanium Ti-6Al-4V ELI samples with variation of voltage and deposition time as shown in Figure 1, while the weight of hydroxyapatite coating layer on material surfaces were indicated in Figure 2. However, there is differences in the coating morphology as a function of the voltage or deposition time. In the voltage variations, it can be seen that the treatment with 8 volt shows the best appearance of coating layer, although in some parts there is an agglomeration of hydroxyapatite particles. The treatment with a lower voltage (5 volt) shows that there are some black spots of the uncoated surface. While at a high voltage (11 volt) shows a fairly thick coating layer.
Increasing deposition of particles on the material surface appears to be influenced by the increase of deposition time. Optimum particle deposition can be obtained with a relative lower deposition time treatment. The results indicate that deposition for 5 minutes is sufficient to produce a good enough coating layer. However, cracks appear in some parts of the layer which tends to be thicker after sintering process. The cracked coating layer can be caused during heating process is due to differences in thermal expansion coefficients and large volume reduction between titanium material and hydroxyapatite [15].
Coating cracks can be avoided by coatings of bilayers using nano/micro-sized hydroxyapatite particles with sintering temperature of 800°C [16]. Heating process with this temperature does not cause phase transformation because the phase transition α to β occurs between 883°C to 960°C [17].

The amount of deposition particles on the surface is influenced by the voltage and deposition time. The increase of the voltage tends to increase of slight deposited particles on the material surface in Figure 2a. The increase in deposition time increases significantly the weight of coating layer in Figure 2b. However, if the applied voltage is too high in a short time, it can result in agglomeration of particles revealing un-uniform particle distribution on the material surface [18], [19]. Therefore, the coating process carried out with low energy in a relatively short time produces a better particle deposition as can be seen by EPD treatment at the voltage of 8 volt for 5 minutes.

Figure 3 (a). Thickness of hydroxyapatite coating by voltage variations (5, 8, and 11 volts) for 5 minutes

Figure 3 (b). Thickness of hydroxyapatite coating by variations in deposition time (5, 8, and 11 minutes) by voltage 8V

Figure 4 (a). Surface coverage of hydroxyapatite coating by voltage variations (5, 8, and 11 volts) for 5 minutes

Figure 4 (b). Surface coverage of hydroxyapatite coating by variations in deposition time (5, 8, and 11 minutes) by voltage 8 volt
The voltage and deposition time treatments give an effect to the thickness of hydroxyapatite coating on the material surfaces in Figure 3. The result revealed that the highest thickness by 11V in Figure 3a have morphology with cracks in Figure 1. In contrast, the treatment with 8V for 5 minutes showed a preferred coating layer (thickness 73.3 μm). This value is in the range of thickness requirements standard for biomedical applications, that is around 50-100 μm [20-22]. The layer can undergo resorption faster with thicknesses below 75 μm but will be delamination with thicknesses beyond 200 μm [23], [24]. Hydroxyapatite coating with a thickness of 50 μm obtained by the plasma sprayed method has an amorphous structure, but it is easily resorbed in physiological environments [25]. The coating obtained in this study visually has a dense structure because it might be affected by sintering after coating. The dense structure will prevent the dissolution of the layer and avoid corrosion of material constituents to the biological environment [26].

Surface covered by hydroxyapatite coating is more affected by voltage rather than deposition time in Figure 4a. The optimum coating properties are not found on high voltage or deposition time. Despite having widest area (surface coverage of 90.5%), deposition with a voltage of 11 volts for 5 minutes produces a thick layer and has a crack in Figure 1. For long deposition time (11 minutes), the hydroxyapatite coating has a too high thickness (120.1 μm) but a low surface area coverage (77.4%). Some accumulation of particles is found on certain parts of the material surface (Fig. 1). However, using low voltage, material covered with relative wide in Figure 4 and thin hydroxyapatite coating (Figure 3a) thus result in even distribution on the material surface in Figure 1. Therefore, coating with a voltage of 8 volts for 5 minutes has a better hydroxyapatite coating with surface area coverage of 82.1% and a thickness of 73.3 μm without cracks and agglomeration.

Figure 5 (a). Roughness of hydroxyapatite coating by voltage variations (5, 8, and 11 volts) for 5 minutes

Figure 5 (b). Roughness of hydroxyapatite coating by variations in deposition time (5, 8, and 11 minutes) by voltage 8 volts

The distribution of hydroxyapatite particles on the surface of the material influences the roughness (Ra) of material surfaces. The higher voltage or deposition time tends to produce the higher roughness value in Figure 5. The Ra of surface for voltage of 5 and 8V is almost the same, 0.86 μm and 0.88 μm, respectively. High roughness allows an increase in the area that will be in contact with the biological environment such as proteins, growth factors or interactions with cells around the material [27]. The rough surface of the hydroxyapatite layer has a direct impact on cellular responses by increasing the adhesion and proliferation of cells involved in the process of repairing bone damage [28]. Thus, roughness by hydroxyapatite has good biocompatibility and triggers osteoblast cell activity on the surface of the material [29]. However, Holthaus et al [29] found hydroxyapatite coatings do not increase osteoblast cell proliferation within 7 days of incubation. Different levels of roughness may have different effects on biological responses. Osteoblasts have a better preference for the surface of the rougher
titanium material with a value of Ra = 0.60 μm to Ra = 7.50 μm [30,31]. The value of Ra = 0.86 μm to Ra = 1.61 in this research shows that the coating produced by the EPD method is predicted to have much better biocompatibility and bioactivity. However, an in vivo test using animal trial is necessary to prove this predictions. This is our next-step works, and it will be reported later.

In the other hand, too high surface roughness can trigger dissolution of coating layers, but the optimum roughness value of hydroxyapatite coating is still unknown [32]. The positive impact of roughness can be lost when the value is very high [12]. In addition, the roughness of the hydroxyapatite coating can decrease due to an increase in sintering temperature due to decreasing in pore size and densification [17]. Thus, optimum roughness was needed for biomedical application encouraging biocompatibility of materials.

The adhesion strength of the coating layer to the material is important characteristic for biomedical application. Applying high voltage or long deposition time seems resulting in the formation of coating layer with poor adhesion to the material surface in Figure 6. Applying high energy produces irregular particle deposition, and long-term deposition makes the charged particles become saturated, so it cannot form a good bond on the material [33-35]. At low voltages with short deposition times in Figure 6, the hydroxyapatite coating tends to bond strongly to the material surface. The coating with the voltage of 8V for 5 minutes shows the lowest percentage of exfoliating area, meaning that the hydroxyapatite layer has a good bond on the material surface. Hydroxyapatite coating which is firmly attached to the material surface, is needed to maintain the structural and functional role of the coating during implantation. Structurally, the hydroxyapatite layer acts as a barrier against the release of toxic constituents from the material into the biological environment and prevents corrosion when in contact with body fluids [36]. The functional role of the hydroxyapatite coating is involved in the body metabolism which initiates bone tissue growth. The hydroxyapatite coating forms a direct bond with bone tissue without fibrous tissue intervention in interfacial tissue and implant material. Encapsulation of fibrous tissue that isolates implant material can trigger implant looseness [37, 38].

Applying high voltages (11V) and long deposition times (11 minutes) produces high thickness, roughness and surface area coverage, but do not result in better coating adhesion as compared to the low voltage and time. Hydroxyapatite coating with impure phase acts as source of crack initiation and transversal cracks over the coating thickness. Iy will be the site of triggering the dissolution of the layer.

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**Figure 6 (a).** Percentage of removed area by cross-cut tape test over hydroxyapatite coating by voltage variations (5, 8, and 11 volt) for 5 minutes

**Figure 6 (b).** Percentage of removed area by cross-cut tape test over hydroxyapatite coating by variations in deposition time (5, 8, and 11 minutes) by voltage 8 volt
The cracks can also reduce the strength of the coating adhesion after immersion in simulated body fluid solution [39]. By using the same material, coating using plasma-sprayed by Oh et al [40] produced coating adhesion strength of 4.5-6.8 MPa. Rojae et al [41] obtained the adhesion strength of the hydroxyapatite coating on magnesium alloys is 4.2±0.3 MPa using sol-gel method.

A stable hydroxyapatite coating is needed to avoid rapid and dangerous dissolution to the body [23]. Debris from coating exfoliation is a risk problem due to it can trigger implantation failure [42]. The adhesion of hydroxyapatite coating to the material surface is also related to the sintering after the coating process [43- 45]. Sintering at high temperatures increases adhesion strength due to the increase of particle diffusion in interfacial parts and triggers diffusion of the bond between the phosphorus element and the material. In addition, adhesion of the coating also can be affected by material preparation before the coating (pre-treatment). Soaking the material with NaOH solution without heating before the coating can increase the coating adhesion and reduce the delamination associated with the increase of osseointegration [46].

4. Conclusions
The electrophoretic deposition method was applied to produce a hydroxyapatite coating on the surface of the Ti-6Al-4V ELI material in order to enhance bioactivity of the alloy, and thus induces osseointegration. Differences in voltage and deposition time influence the surface characteristics including layer thickness, surface coverage, layer roughness and the adhesion strength of the coating layer. The EPD process with a voltage of 8V for 5 minutes resulted in the best performances with a coating roughness of hydroxyapatite layer (Ra) as much as 0.88. The removed area after the cross-cut tape test is 2.25%, which means adhesion strength between the coating and the materials is high enough. A relatively high hydroxyapatite mass (0.3 mg), is covering the material surface with a surface coverage of 82.1%, and the average coating thickness is 73.3 μm. The important things is almost no cracks are found in the surface layer. The thickness coating layer meets to implants requirement between 50-100 μm. Such kind of coating layer characteristics are strongly believed to increase bioactivity, biocompatibility and thus enhancing osseointegration capacity of prosthetic medical implants. However, an animal trial is necessary to carry out for proving this prediction. This is our next-step works, and it will be reported later.

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