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# Hydroxyapatite Coating on Titanium Alloy Ti-6Al-4V with Electrophoretic Deposition (EPD) for Dental Root Application

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Abstract— An  $\alpha+\beta$  type titanium alloy, Ti-6Al-4V, has been coated with hydroxyapatite through electrophoretic deposition (EPD) method to improve quality of the alloy surface, in order to fulfill bioactivity requirement for orthodontic application as dental roots. The deposition process was conducted by EPD at different voltages (2 volts, 5 volts, and 10 volts) and time (2 minutes and 5 minutes). After deposition, the material was heated at temperature  $700^{\circ}$ C for 1 hour using a vacuum furnace. Coated samples analysis was conducted by scanning electron microscope (SEM) and energy dispersive X-ray (EDX) to examine coating layer morphology and its chemical composition, respectively. Experimental results showed that the voltage and time deposition gives different effects to surface coverage and thickness of hydroxyapatite layers. Optimum layer for dental roots is obtained from the voltage of 5 volts for 5 minutes with 100% surface coverage value and  $45.55\mu$ m in thickness. With low voltage and short deposition time for making a uniform coating layer, this process is much cheaper than other processes, and it is predicted to be favorable for improving osseointegration of dental roots.

Keywords—hydroxyapatite; Ti-6Al-4V; electrophoretic deposition; dental roots

## I. INTRODUCTION

Medicine treatment for dental problems has been done either through substitution using partially or totally of biomaterials, like as dental root applications. Metal-based biomaterials for dental root implant, titanium alloy Ti-6Al-4V, still giving a problem such as less osseointegration owing to loosening for long time implantation. This is affected by decreased of interaction between implants and dental tissues that may lead to implant failure [1]. Materials Ti-6Al-4V have good mechanical characteristics for biomedical application, that are biocompatibility, nonmagnetic, high yield and tensile strength, low Young's Modulus, and excellent corrosion resistance [2]. Challa et al. [3] reported that TiO2 layers on titanium surface categorized as a toxic constituent by International Agency for Research on Cancer (IARC). Biological responses for titanium show fibrous encapsulation that may effect for micro movement and decreases mechanical properties which impact for reduce integration with bone tissues [4], [5]. Therefore, surface modification for Ti-6Al-4V material through coatings method with hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] aims to improve osseointegration. Osseointegration was indicated as the interaction between implant material and bone tissue in achieved new bone ingrowths for the healing of tissue defects. Moreover, the coating layers also function as protection from releasing debris particles or harmful ions from metal that promotes infection through disrupting of metabolisms and implant failure [6].

Using of hydroxyapatite (HA) as biomaterial coatings are performed based on its biocompatibility and bioactive properties that could be bond chemically with bone tissue to achieve dental root osseointegration. Osseointegrated hydroxyapatite can be depended on coating methods. Plasma spraying is commonly used for coating method used high temperature above the melting point of hydroxyapatite

(1550°C). High temperature would make the possibility of HA phase transformation and results in calcium phosphate amorphous phase so that decreases coatings quality [7], [8]. Electrophoretic deposition (EPD) can be used as a favorable method in order to overcome the transitions of hydroxyapatite composition. The principle of this method is migration process of charged particles within suspensions influenced by electric fields, so that agglomeration and deposition occur on the material surface that used as charged electrode [9,10]. Treatments were carried out in controlling condition in order to prevent the change of mechanical properties for both materials and coatings [11]. These techniques can be applied for complex and variance material such as composites, ceramics, and organic materials; recruits simplicity instrument with low cost; and produces controlled homogeneous coating thickness and cristanility [10], [12]-[13]. Moreover, this method can be done in short time and implemented for materials that used in biomedical application [14]-[16]. The procedure has not effected for composition and characteristic of hydroxyapatite coatings and substrate materials [13],[14],[17]. However, heat treatment or sintering is needed to improve density and adhesion of coating [18] in considerate thermal expansion coefficient of coating and substrate.

There are many impact parameters, such as voltage, time, pH value, and solvent medium that influence coating characteristics [19]-[25]. Several researches had been using the wide range of deposition voltage, which is approximately 2V - 500V for different deposition time that is 3 seconds until 90 minutes. Rad et al. [6] using constant high voltage for coating with EPD results in poor morphology and mechanical coatings. Higher voltage would result nonuniform, non-adhesive, and high porosity is promoting cracks coatings characteristic [19,20,26] deteriorating the quality of coatings [23]. In another case, Drevet et al. [21] observed that low voltage (5V) in variant deposition time for hydroxyapatite coating does not make possible to migrate the particles in suspensions properly. It means low voltage supply insufficient energy for moving hydroxyapatite in suspensions. Research conducted by Shahrezaei et al. [27] using 2V in 30 minutes for hydroxyapatite coating on magnesium alloy material results uniform coating with fine structure. A similar condition conducted by Santillan et al. [28], voltage <2V produces properly non-adhered layers to the substrate. The low threshold voltage that is enough for hydroxyapatite deposition is still unknown. Furthermore, time deposition is a less important factor contributing to coating [29]. However, it plays a role as a supplementary factor for variant coating quantity. Yildirim et al. [30] report that the lower voltage and longer deposition time will advantage for proper coating. Therefore, the study is still needed to find the proper parameters for hydroxyapatite coatings on a  $\alpha+\beta$  type titanium alloy, Ti-6Al-4V, as dental root application by EPD method.

#### II. MATERIALS AND METHODS

Titanium alloy discs, Ti-6Al-4V, with 10 mm diameter and 5 mm thickness were used as a substrate in this study. Samples abraded by using silica carbide (SiC) paper with 600-grit and 1000-grit followed by polishing machine for facilitating coatings. The deposition area carried out on the one side of materials. The material was then immersed and cleaned in distillation water, and methanol used ultrasonic bath (pH 7.33) for 15 minutes and followed with NaOH solution for 1 hours. The samples were air dried with Stirring Hot Plate machine for 5 minutes.

The EPD suspension was prepared by adding 1.25 gram hydroxyapatite powders (Sigma-Aldrich) to 50 mL ethanol solution. The pH value was adjusted to 4.0 by addition of HNO<sub>3</sub> solutions. Instrumental for EPD consisted of gun glue, copper wire, graphite, and digital power supply. The graphite and titanium were anode and cathode, respectively. The deposition process was carried out by different deposition voltages and times. After coating, samples were air dried at room temperature overnight. The as-deposited coatings sample heated used vacuum furnace (High-Temperature Vacuum Tube Furnace GSL-1100) in order to increase the density of coatings. The sample then heated at temperature 700°C with heating time for 660 minutes, holding time for 60 minutes and annealing time for 720 minutes and furthermore, the heating rate was 60°C/minute or 1°C/second [31].

Morphology analysis of coating surface was examined using an optical microscope (Olympus GX71) and scanning electron microscope (Hitachi S3400N operating at 15.0 kV, in conjunction with a detector for energy dispersive X-Ray analysis (Horiba). The X-ray analysis was conducted for quantitative of Ca/P ratio.

### III. RESULTS AND DISCUSSIONS

Fig. 1 shows morphology characteristic of hydroxyapatite coating on Ti-6Al-4V material surfaces, where material surface is covered up by hydroxyapatite coating. The coverage surface increases along with applied voltage following by excessive deposition time, and it will affect the increase in coating thickness. Higher thickness by longer deposition time will be peeling off easily that is caused by less adhesive of the coating. The low voltage and less deposition time resulting in the uncoverage area or bare surface that indicates it is not capable of depositing materials on the substrate. Probably, it caused by low energy and the other parameters used in the electrophoretic deposition such as pH and solvent medium.

The higher coverage surface until 100% can be achieved at a voltage of 5V for 5 minutes and 10V for 2 minutes (Fig. 2). At the voltage 2V/2 minutes, 5V/2 minutes and 2V/5 minutes, hydroxyapatite has not covered up substrate surface, whereas, in 10V/5 minutes, the coating has thick layers that break up quickly. Namely, the low voltage and short deposition time, incapable of depositing hydroxyapatite particles, so almost the entire round material surface does not cover up. The high voltage produces high coverage

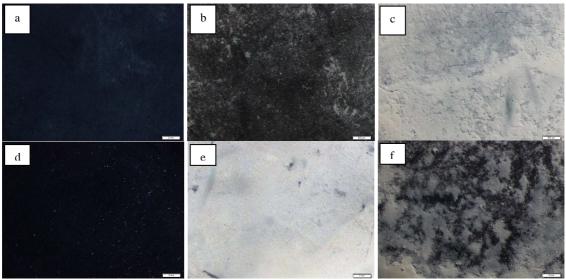


Fig. 1 Scanning electron microscope of hydroxyapatite-coated titanium disks at different voltage and time (a. 2V/2 minutes; b. 5V/2 minutes; c. 10V/2 minutes; d. 2V/5 minutes; e. 5V/5 minutes; f. 10V/5 minutes)

and thick coating, nevertheless it is easy to be detachment because of the weakness of bond between particles of coatings. This condition can be overcome by heat treatment. Molaei *et al.* [14] suggest the low voltage and long deposition time as desirable parameters for uniform coatings. In contrast, Yildirim *et al.* [30] acquire the high voltage and short deposition time as a preferable condition for hydroxyapatite coating. The current study discovered, by lower voltage and low deposition time, material surface already covered up over hydroxyapatite. In morphology, the coated surface has rough topography than plain substrate surface. It may associate with osseointegration and interact with bone tissue around the implant surface in vivo [32] reaching of the healing process.

The voltage has certain effect for coating characteristics in morphology and roughness. Current potential from the electric field will be moving particles in suspensions resulting certain layer thickness on substrate surface [12]. The deposition rate will increase over with the increased voltage. However, the quality of coating depends on the voltage rate. High voltage results in an electrophoretic velocity of particles quickly and may cause turbulence. The smallest particles will deposit at first and followed by larger size particles [23]. Thereby, particles can be arranged and packed improperly in little time on substrate surface resulting in high porosity and agglomeration of small particles [23], [33], [34]. After sintering, the coating will be showing the cracking and less adhesion [19] in consequence of shrinkage and densification. Meanwhile, the low voltage will migrate and deposits particles properly in the substrate surface. However, the too low voltage cannot migrate larger particles due to insufficient energy [14]. In this work, applied voltage at 5V, particles migrate in suspension and deposit on the surface resulting even and proper thick coating as seen in Figs. 1 and 2. Agglomeration and crack were not found, indicates as a proper voltage for hydroxyapatite coating parameters and desirable biomedical application [10].

The voltage associated with hydrogen evolution on the cathode, which promotes pore formation during EPD process.

Porosity will initiate shrinkage and densification because of heat treatment and results cracking [18], [35]. The crack propagation and less adhesion were commonly discovered in the thick coatings [18], [36] more than  $20\mu m$  acquired by high voltage [35]. The exfoliation was not found in the thin layers of coating [37]. The thickness of hydroxyapatite in this study was thin that is approximately  $0.00\mu m$  -  $49.82\mu m$  (Fig. 3). Furthermore, the short time cannot produce a coating that covered up a round of the material surface properly. As if the voltage affects the coverage of coating, deposition time correlates with the thickness of the coating. In this study, the thickness increases along with the long deposition time.

Through by EPD method, the thickness of coatings layers can be obtained about 0.1µm - 100µm [10], [18]. If the coating layer is thick, delamination and degradation may be occurred that producing unstable implant and promote implant failure. de Groot et al. [38] reports that the thickness of coating over 100µm or excessive lead to delamination and fragmentation with worse mechanical properties such as fatigue failure, poor adhesion, and quick dissolution. Meanwhile, the thin coatings around 50µm have a stronger fixation with living things. In contrary, Furlong et al. [39] suggest the better coatings thickness for a prosthesis that is approximately 200µm due to one-fourth of the layers would be reabsorbed for osteogenesis. Hydroxyapatite coatings should be reabsorbed on the fluid body and substituted by new tissues immediately after implantation [40], [41]. Hydroxyapatite coating will improve bone growth and directly interact with living tissue [30]. Some research reported that the optimum hydroxyapatite coatings for biomedical application around 50µm -100µm or less [41]-[43]. The advantage of thin coatings is to prevent alteration of mechanical properties such as fracture and topography that will effect in cell, proteins or molecular of the body. In addition, it will promote osteogenesis efficiently [44]. The thin coating may modulate bone tissue metabolism for the healing process.

The current study, by voltage 5V for 5 minutes, the coating thickness of hydroxyapatite is 45.55µm. Xiao et al.

[17] observe the hydroxyapatite coatings thickness is around 50µm obtained from deposition at voltage 30V for 1 minute. Through voltage 30V for 10 minutes, Hussain et al. [45] obtain homogeneous, adhesive, and uniform coatings. Drevet et al. [21] produce hydroxyapatite coatings optimal were acquired by voltage 10V for 10 minutes. Maleki-Ghaleh et al. [18] showed that the optimum voltage in hydroxyapatite coatings by EPD method was 60V for 2 minutes. Li et al. [36] experimented coatings by EPD method with the optimum voltage is 30V for 1 minutes. The voltage is around 220-360V for 10 seconds may produce the coating thickness is approximately  $25\mu m$  -  $65\mu m$  and the crack rate is about 32% [26]. Based on these studies, it assumed as if coatings characteristic can be controlled with the variant voltage and deposition time. The optimum coating's thickness for biomedical application by EPD method can be acquired with the range voltage is approximately 5-60V for 1-10 minutes. In suggestion, the suitable thickness for implantation is around 50µm.

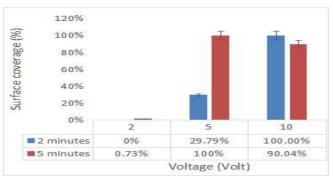


Fig. 2 Surface coverage of hydroxyapatite-coated titanium disks

Based on Hamaker equation, the deposition rate of hydroxyapatite coating will improve along with prolonging of deposition time [45], [46]. However, Li et al. [36] found that the deposition rate decreases in line with the addition of time. Corni et al. [12] explain the logarithmic correlation between a variance of time and deposition layers. Increasing of deposition rate found in the early deposition time (0-4 minutes) and decreasing occurs progressively to reach the lower rate in the certain period. This is come off in spite of deposited particles have effect decline of current potential in suspension. The long increasing of times will affect decrease current density, so saturation occurs. This decline can be influenced by insulator hydroxyapatite ceramic materials [18], [45], [47]. Increasing of resulted thickness along with increasing of time can improve coating resistance and decrease current flow. After achieving the certain time, migration of particle will reduce due to voltage saturation in a long time. It means the voltage and deposition time would influence the coating thickness [45]. The long time-result lead to performance to particle resistance for current potential and thereby surface uncovered properly; crack propagation when heat treatment was given; and coating degradation since implantation [11], [13], [36]. This phenomenon can be explained that increasing hydrogen evolution by progressively increasing voltage in long deposition time. Therefore, the proper parameters are needed to get the better coating characteristic as the advantage of electrophoretic deposition method.

The advantage for coatings by EPD method is the proper quality of coatings can be indicated by the phase transformation does not take place because it uses relatively low temperature during EPD process. Rad *et al.* [6] proved that EPD does not affect the decomposition of hydroxyapatite. Therefore, the other parameters, such as heat treatment may give influence in coatings composition that is calcium and phosphor ratio (Ca/P) as shown in the Fig. 5. The value of Ca/P ratio for voltage 2V 5V and 10V, respectively, are 1.604; 2.018 and 1.97. The ratio value almost approaches the standard of Ca/P ratio, which is 1.67 for biomedical application.

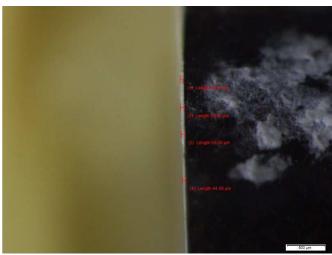


Fig. 3 Scanning electron microscope of hydroxyapatite-coated thickness at 5V for 5 minutes deposition

Basically, sintering aim to increase the bonding of particles in coating layers within the atomic or molecular interaction. The heating may affect the strength by densification or recrystallization mechanism of particles [48]. Therefore, sintering was conducted under the transformation temperature for hydroxyapatite. Heat treatment with temperature 700°C may be influence Ca/P ratio of hydroxyapatite coatings. During sintering, diffusion of phosphor to materials can affect partial decomposition of hydroxyapatite coating forming tetra calcium phosphate (TTCP) and tricalcium phosphate (TCP) with high Ca/P ratio. Minor phase TCP from HA decomposition [26], can be affected by partial dehydration mechanism or metal ion change at interfacial during sintering process [21],[49]. The extension reaction will result in the poor coating adhesion.

The strength of coatings may be influenced by heating rate during sintering. By faster heating rate, the time achieved for sintering is low which means densification is not reached perfectly so it sill remaining pores. In consequences, decreasing of adhesion strength occurred between particles of coating layers caused by less contact and weakness bond. Through different materials, heating rate 5°C/minutes and 10°C/minute can be improved hardness and strength of iron powders, respectively. The current study using heating rate 60°C/minutes produce less adhesion or peeling off of coating layers. In fact, the adhesion strength is caused by sintering procedures typically heating rate [50].

The mechanical properties of coating layers also can be influenced by sintering temperature. A few study reported

the increase of sintering temperature about 875-1000°C with the optimum temperature 975°C could improve adhesion strength of hydroxyapatite coatings on titanium materials [51]. However, the enhancement of temperature above 875°C can affect hydroxyapatite decomposition resulting tricalcium phosphate (TCP) phase. It could be reduction strength (mechanical properties) implantation in vivo [8], [49]. A TCP phases work out fast dissolution and will bind with bone tissue so decline adhesion strength with the material [52]. This is the crucial problem when applied in the biomedical application so needed the effort to control the phase formation. The TCP phase will be formed when sintering temperature achieved 1200°C [49], [51]. However, low temperature around 875°C will affect material ions migration to coatings and promote TCP formation [21], [26], [35], [49].



Fig. 4 Thickness curve of hydroxyapatite-coated titanium

Sintering conducted at above 1000°C will promote degradation of mechanical properties (phase transformation, grain growth, and surface oxidation) that influence for material biocompatibility [35]. However, Ma et al. [53] did not find of formation of a new structure at sintering temperature 1000°C, and there are a little amount of TCP and agglomeration so results in denser coatings. Analysis of thermal stability of hydroxyapatite coatings shows that heating until 800°C affects the loss of coatings weight about at PVA/HA coatings. It indicates 7.05%-18.01% dehydroxylation of HA [45]. Hussain et al. [45] and Wei et al. [51] reported the increase of shear strength without sintering at PVA/HA coatings. At high temperature, HA work out decomposition in an early step that is signed by dehydroxylation (900°C in room and 850°C at water-free atmosphere) and the next step resulted in tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP) [54]. At a temperature of below 1350°C, HA strength decreases significantly [55].

Furthermore, pH value and alcohol solvent may be had effect for acquired coating characteristics. pH value has associated with zeta potential which indicates suspension stability [17]. Zeta potential will make a movement of charged particles in suspension towards the opposite of charged electrode [14]. Stable suspension of ethanol for HA coating is approximately pH value 2 (pH < 4) or around 5

pH, because it has high zeta potential [12], [14], [19]. Over this value, hydroxyapatite was found in smallest particle size indicating well-dispersed particles in the suspension have high mobility for a deposit toward the substrate. Larger particles will disturb deposition owing to agglomeration occurrence [16]. Thus, higher zeta potential by decreasing of pH value will result in high deposition rate [14].

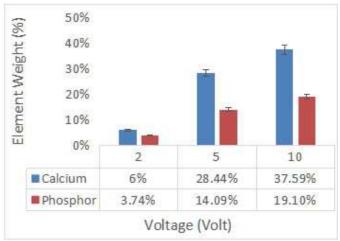


Fig. 5 Element weight of calcium and phosphor on hydroxyapatite-coated titanium disks at different voltage

The current study uses ethanol as the suspension medium. Increasing ethanol concentration will decrease ceramic mobility due to the formation of H<sup>+</sup> in suspension that has higher mobility [28]. Xiao *et al.* [17] explain using of n-butanol as a proper medium for hydroxyapatite suspensions based on chemical reaction. However, hydroxyapatite particles coagulate quickly in n-butanol without addition TEA as a dispersant. The important thing for noticed, zeta potential influenced by medium suspensions [12] will affect the deposition rate [22].

Electrophoretic deposition method was influenced by complex parameter so can be resulting variant of coating properties. In the study, the low voltage and low deposition time can result in proper coating characteristics already. The other parameter, such as pH value, medium solvent, and sintering temperature can improve the quality of coatings. Meaning, this method is effective and efficiencies for using coatings of hydroxyapatite on a metal surface like titanium.

# IV. CONCLUSIONS

Using of Ti-6Al-4V materials in biomedical application still giving problems in health. In order to improved quality, coatings on surface materials use bioactive and biocompatibility materials. Hydroxyapatite coatings on Ti-6Al-4V materials for dental root fixation can be acquired with electrophoretic deposition (EPD) method. This method is efficient and effective to produce high-quality coatings. In the current research, with pH and the medium solvent was controlled, voltage and time were used as parameters and sintered at 700°C. The obtained coatings characteristic have a thickness approximately 45.55µm and surface coverage 100% from voltage treatment at 5V for 5 minutes. Voltage has effect for surface coverage and deposition time influences the thickness of the coating. Heating by sintering can produce shrinkage and agglomeration of thick coating

that associates with high voltage and long deposition time. The thick coating may cause delamination and degradation, which is, promotes implant failure as in vivo implantation. By thin coating, osseointegration can be achieved due to the interaction of bioactive hydroxyapatite with a stable coating in tissue growth. With low voltage and short deposition time for making a uniform coating layer, this process is much cheaper than other processes, and it is predicted to be favorable for improving osseointegration of dental roots.

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