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Electrophoretic Deposition of Hydroxyapatite/Chitosan Coating on Porous Titanium for Orthopedic Application

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Abstract: This work is focused on addressing bioinert properties of titanium as orthopedic implant problems by applying surface modification to porous titanium. In this research, electrophoretic deposition of hydroxyapatite (HA) and chitosan (CS) was done on porous titanium prepared by space-holder powder metallurgy. 1 wt% of HA and 0.5 wt% of CS in acetic acid is used as the electrophoretic solution. Deposition voltage was varied in a range of 5–7 V, and the electrophoretic time was between 10 and 15 minutes. Coating morphology, deposition weight, and the adhesive properties of the HA/CS layer were observed in this experiment. 7V-10 minutes specimen and 7V-15 minutes specimen gave the best result due to large HA/CS deposits, covering pores, homogeneous, and having the best adhesivity. The coating quality is increasing in line with the increasing voltage and the electrophoretic time.

Keywords: Electrophoretic, Titanium Porous, Hydroxyapatite, Chitosan.

1. Introduction

In a study by the Ministry of National Development Planning/Bappenas entitled "Indonesian Population Projection 2010-2035", the projection of the Indonesian population has increased every year. Indonesia's population was 238.5 million people in 2010, 255.5 million people in 2015, and 271.1 million in 2020. It will reach 284.8 million people in 2025, 293.4 million in 2030, and 305.6 million in 2035[1)]. The increasing population of Indonesia will increase the mobility of the Indonesian population. Assisted by the development of technology that can help human activities, it can also cause several problems, including congestion, increasing pollution levels, and accidents that can even cause death. The Ministry of Health explained that cases of bone injuries in Indonesia continue to rise. As many as 8 million people experienced bone fractures, the highest contributor to bone fractures was caused by traffic accidents as much as 46.2 percent since 2013[2)]. According to Indonesia-Statistics (BPS), the need for implants in Indonesia was worth IDR 20 trillion in 2016, it rose to IDR 23 trillion in 2017, and it increased to IDR 27 trillion in 2018[3)] . Hence, the development of implant is increasing, not only in Indonesia, but also globally [4-6)].

Titanium is a commonly used biomaterial because it has suitable characteristics, such as corrosion resistance, good mechanical properties, and fracture toughness[7-9)]. Titanium still has its limitations due to the high value of Young's modulus. Therefore, it can cause a stress-shielding effect which can be harmful to the implant itself and humans. Adverse effects such as bone resorption may require revised surgery which reduces the material usage[10)]. With these limitations, one solution is to use a porous titanium material. Porous structures can solve the stress-shielding effect caused by the high Young's modulus of bulk titanium. The porous structure will reduce the stiffness and the density of the bulk metal. Hence, titanium can have better characteristics to be used as implant materials[7)]. Further, titanium also still has limitations because its surface has low bioactivity and osseointegration properties. It can inhibit bone growth properties and long-term stability. Therefore, a surface treatment is needed to obtain the desired results. One of the surface treatment processes is the electrophoretic deposition process. Recently, several coating methods have been used; such as plasma spraying, IOM beam sputtering, sol-gel, electrophoretic deposition, electrochemical deposition, and others[11)]. Electrophoretic deposition is a simple technique that can make films and coatings on a complex substrate[10)]. Titanium is a material with low bioactivity and osseointegration, so that surface treatment is needed to overcome these limitations. Hydroxyapatite can be used as a coating material to overcome the low osseoinductive of titanium[11)].

Hydroxyapatite is generally used for bone implants because it has similar chemical properties with bone tissue[12] which makes it has excellent bioactivity and biocompatibility[13]. Having similarities to human bone and the ability to promote osteoblast formation, hydroxyapatite coating can contribute to bone implants with increased bioactivity and new bone formation[14]. Meanwhile, chitosan is an antibacterial material and has a superior film-forming property. In alloys, chitosan can improve the properties of the substrate and reduce the brittleness of hydroxyapatite[15]. The objective of this research is to study the formation of a hydroxyapatite/chitosan (HA/CS) composite coating layer on porous titanium by the electrophoretic deposition method. The processing parameter such as applied voltage and time are observed to create a homogeneous and evenly deposited layer to achieve high adhesive properties.

2. Materials and Methods

Porous titanium substrates were prepared by using space-holder powder metallurgy. NaCl powder (20 wt%) was used as the space-holder. The powders were mixed with the commercially available titanium powder followed by cold compaction at 560 MPa pressure. The green bodies were preheated at 800 °C for 2 hours. Subsequently, the sintering process was conducted under Argon atmosphere at 1000 °C for 2 hours. The substrates were ground on the emery papers following a sequence of #400, #600, #800, and last #1000. Then the samples were immersed in wet alumina for 5 minutes. After being immersed in wet alumina, the samples were ultrasonicated (15 minutes in the acetone and 15 minutes in the ethanol). Afterward, the samples were immersed in ethanol until the electrophoretic process.

Hydroxyapatite nanopowder (particle size less than 200 nm) and chitosan powder (medium molecular weight) were used as the starting powder to prepare the nanocomposite HA/CS coating layer solution. Chitosan (0.5 wt%) was dissolved in distilled water containing 1% acetic acid in a beaker glass. Hydroxyapatite powder (1 wt%) was added into the solution then stirred for 30 minutes until the suspension was homogeneous (pH=4.4). Further, the electrophoretic process was performed by assembling porous titanium (cathode) and two Pt electrodes (anode) in a beaker glass. During the electrophoretic process, the suspension was constantly stirred to prevent sedimentation. The position of the porous titanium is in the middle of Pt electrodes with a distance of 1.5 cm. The electrophoretic process was done at 5, 6, and 7 V for 10 and 15 minutes. After the electrophoretic process, the samples were dried for 24 hours at room temperature. Sample characterization was done using a microscope to get visual observations, scales to get the deposition weight of the coating, also adhesive tape and scrubber to determine the adhesive properties of the coating on the porous titanium. The schematic for the electrophoretic deposition process is shown in Figure 1.

Fig 1: Schematic setup of electrophoretic deposition process

3. Results and Discussion

3.1 Electrophoretic Deposition on Porous Titanium

Figure 2 shows the surface of the sample after the preparation process. Grinding on the emery paper was able to remove the dirt from the specimens so that the substrates were ready to be used for the electrophoretic process. Further, after the cleaning process using an ultrasonic cleaner, the samples were immersed in ethanol until the electrophoretic process. During the electrophoretic process, the occurrence current is tabulated in Table 1 and Table 2.

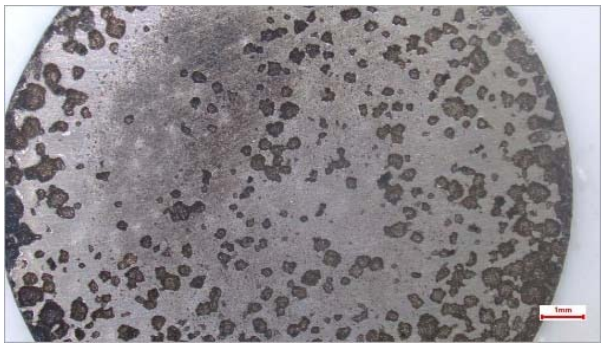

Fig 2: Porous Titanium Before Electrophoretic

Table 1. The Electric Current During Electrophoretic Deposition for 10 Minutes

Time (Minutes)	5 Volt	6 Volt	7 Volt
1	0	0	0.01
2	0	0	0.01
3	0	0	0.01
4	0	0	0.01
5	0	0	0.01
6	0	0	0.01
8	0	0	0.01
9	0	0	0.01
10	0	0	0.01

Table 2. The Electric Current During Electrophoretic Deposition for 15 Minutes

Time (Minutes)	5 Volt	6 Volt	7 Volt
1	0	0	0.01
2	0	0	0.01
3	0	0	0.01
4	0	0	0.01
5	0	0	0.01
6	0	0	0.01
7	0	0	0.01
8	0	0	0.01
9	0	0	0.01
10	0	0	0.01
11	0	0	0.01
12	0	0	0.01
13	0	0	0.01
14	0	0	0.01
15	0	0	0.01

The electric current can be observed through the DC power supply during the electrophoretic process. The electric current has a role in the electrophoretic process because a stable electric current will lead to good coating results. In contrast, an unstable electric current will affect the morphology of the deposit results[16]. Meanwhile, the suspension is also influenced by the pH condition. Since chitosan solubility is pH-dependent, it has an optimal pH for protonation. When the pH value is below 6 chitosan will undergo protonation. Yet, when the pH value is higher than 6.5, it will be deprotonated and become insoluble. Moreover, if the pH value is too high, it will reduce chitosan's electrostatic repulsion to form an inter-polymer that creates fibers, films, or hydrogel[17]. The pH value of the suspension before the electrophoretic deposition is shown in Table 3.

Table 3. The pH value of suspension before electrophoretic deposition

Specimens	pH
5 Volt- 10 Minutes	5.6
5 Volt- 15 Minutes	5.7
6 Volt- 10 Minutes	5.7
6 Volt- 15 Minutes	5.8
7 Volt- 10 Minutes	5.7
7 Volt- 15 Minutes	5.8

Chitosan will dissolve in an acidic solution (pH<6) hence the amine groups of chitosan are protonated and has positive charges[18]. In another reference, it is also stated that at pH values less than 6.3; chitosan will become positively charged due to protonation of the primary amino groups so that it can dissolve in water[19]. The protonation reaction occurs according to equation 1.

$$CS\text{-}NH_2 + H_3O^+ \leftrightarrow CS\text{-}NH_3^+ + H_2O \quad (1)$$

The results of the sample after drying are displayed in Figure 3. For each variable, there is a white layer covering the porous Titanium sample. It shows that the electrophoretic process has been successful. It can be seen that there is a hydroxyapatite/chitosan coating layer deposited on the porous titanium sample. Hydroxyapatite and chitosan can be deposited evenly at voltages of 5, 6, and 7 Volt, likewise at 10 or 15 minutes. From Figure 3 (a-f), there is no clear evidence of crack at the coating layer. The morphology of the coating for the entire sample is smooth and pore-free.

The coating layer can be electrophoretically deposited on porous materials by making an inner layer. To obtain good results, the particles that can block the pores must be cleaned first[20]. Generally, when liquid droplets come into contact with the pore surface, there are two mechanisms. First, the process of spreading to the entire surface of the pore surface, and second, penetrating or experiencing absorption into the pore structure[21]. The theory of the electrical double layer has been recognized and understood for investigations of colloids and interface science to predict and determine the distribution of electric charges at solid-liquid interfaces. Charged molecules will move towards the cathode and can be explained in terms of the electrical double layer mechanism[16]. The interactions between charged particles are governed by the overlap in the diffusion layer, and the potential that is most relevant to the interaction formed between the stern layer and the diffusion layer is compared to the potential at the particle surface. This potential difference between the sternum and the diffusion layer is called the zeta potential. Zeta potential plays a role in the electrophoretic process, which includes stabilizing the suspension by determining the intensity of repulsed interactions between particles, determining the direction and speed of particle migration during the EPD, and then determining the green density of the deposit. The interaction between the electric field and the ions accompanied by the displacement of particles from the double layer causes a tangential velocity for the fluid from the diffusion layer. The slip velocity at any point on the surface was described by Helmholtz for electro-osmotic[22]. If the electro-osmotic is neglected, it will decrease particle mobility. In an electric field, the insulating wall will induce an electro-osmotic flow, the direction of which depends on the zeta potential. For open-pore surfaces, the electro-osmotic flow has a uniform velocity profile and a neutral particle immersed in the fluid will be dragged by the electro-osmotic flow and move at the same speed[16].

In the electrophoretic process of porous materials, when the material is added into the suspension, the suspension fills up to the pore gap, indicated by the release of bubbles caused by the suspension entry at the pore gap. In this case, the suspension containing hydroxyapatite and chitosan will be in contact with the porous titanium followed by the spread over the entire surface of the material, assisted by the electric current. Hence, the hydroxyapatite/chitosan

composite can penetrate the pores and sediment on the surface. Hydroxyapatite/chitosan composite will continue to be deposited and precipitated during the electrophoretic process. Meanwhile, for the non-porous material, when the substrate is added to the solution, there are no bubbles caused by the suspension entry to the pore gap so that the hydroxyapatite/chitosan coating will be deposited easily with the help of the given current.

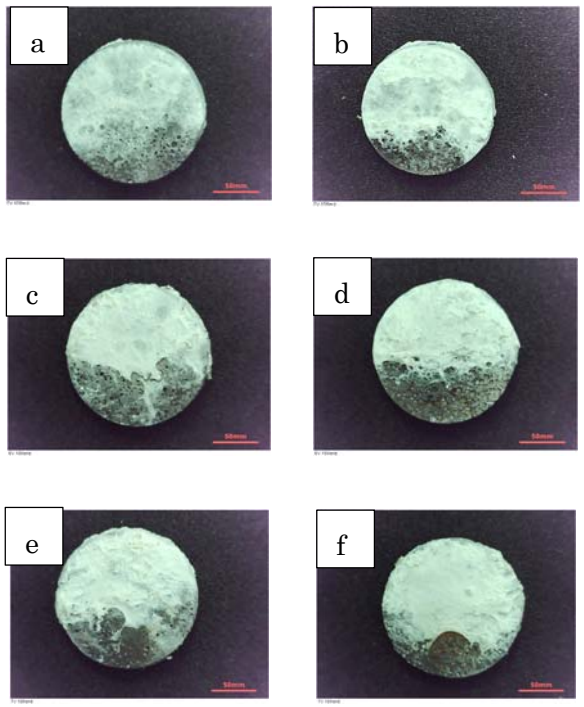

Fig 3: Result of Electrophoretic a) 5V-10Min, b) 5V-15Min, c) 6V-10Min, d) 6V-15Min, e) 7V-10Min, f) 7V-15Min

3.2 Effect of Voltage to the Electrophoretic Deposition on Porous Titanium

Figure 4 shows the deposition weight of hydroxyapatite/chitosan composite on the porous titanium. It can be observed that using 5 V-10 minutes electrophoretic process, the deposited HA/CS was 5.95 mg/cm²; at 6 V-10 minutes, the deposited HA/CS value was 12.98 mg/cm²; and at 7 V-10 minutes, the deposited HA/CS value was 26.67 mg/cm². Increasing voltage is in line with the increase of deposition weight for 10 minutes duration of electrophoretic deposition. While for other specimens, at 5 V-15 minutes electrophoretic process, the deposited HA/CS was 8.42 mg/cm²; at 6 V-15 minutes, the deposited HA/CS value was 14.74 mg/cm²; and at 7 V-15 minutes, the deposited HA/CS value was 30.18 mg/cm². These results are similar to other research; as the voltage increases, the deposition period on the cathode also increases[23]. However, if the applied voltage is too low, the layer is difficult to form because the low voltage causes the particles to migrate slowly. Further, the low voltage might also cause broken layer formation in some areas of the specimen[19]. On the other hand, high voltage can cause faster movement of the particles so that the coating can be formed quickly. But applying high voltage can cause hydrogen evolution so that the bubbles are massively formed resulted in an inhomogeneous coating layer, a crater-like surface coating layer[24].

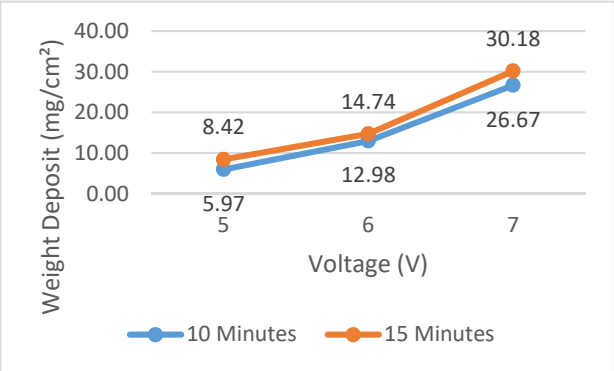

Fig 4: Deposit Weight per Area Based on Voltage

3.3 Effect of Time to the Electrophoretic Deposition on Porous Titanium

In addition to the applied voltage, time in the electrophoretic deposition process is another crucial factor. The longer time of electrophoretic deposition, the higher mass of the coating layer is deposited on the substrate. Time-dependent on the electrophoretic would give a different thickness of the coating layer. Based on Figure 4, at the same applied voltage, the deposit weight per area will be increased by the increase of time. For 5 V-10 minutes to 5 V-15 minutes electrophoretic, there will be an increasing deposit weight from 5.97 mg/cm² to 8.42 mg/cm². For 6V-10 minutes to 6 V-15 minutes electrophoretic, the deposit weight is increased from 12.98 mg/cm to 14.74 mg/cm². Last, for 7 V- 10 minutes to 7 V-15 minutes electrophoretic, the deposit weight is increased from 26.67 mg/cm² to 30.18 mg/cm². It is shown from the curve that the increasing time up to 5 minutes has a lower increment deposit weight than the increasing voltage. The increasing deposit weight indicating the increase of coating thickness.

3.4 Effect of Time and Voltage to the Adhesive Property of Hydroxyapatite/Chitosan Coating

Figure 5 shows the photograph of the coating layer after the adhesive test (cross-test tape), while Table 4 shows the interpretation of the adhesive property of the coating layer. Based on ISO 2409, there are six categories in the cross-tape test results. The resulting thickness can increase the adhesive resistance[25].

Based on Figure 5(a), the quality of coating for the sample with 5 V-10 minutes electrophoretic is classified as "3", where the coating has been peeled off along the cut edges partially or completely in a large band, and/or has been partially or completely peeled off entirely on a different part of the box. In the cross-cut, the affected area is more than 15 percent but less than 35 percent. Figure 5(b) and Figure 5(c), which are the results of the 5 V-15

minutes 6 V-10minutes electrophoretic process, these coating layers are categorized as "2", where the coating has peeled off along the edges and/or at the intersection of the cuts. In the cross-section, the affected area is greater than 5 percent, and less than 15 percent. Figure 6 (d) shows the result of a 6 V-15 minute electrophoretic that is classified as category "1", where small pieces of the layer at the junction of the cuts are peeled off with a value of less than 5 percent. Figure 6 (e) and Figure 6 (f) show the results of 7 V- 10 minutes and 7 V-15 minutes electrophoretic samples, which are categorized as "0", where the cut edges are smooth; no lattice squares are detached. The quality of the coating that has good adhesion results is due to the high surface area and the phenomenon of physical locking between hydroxyapatite and titanium[26]. The good adhesion strength is due to the homogeneous microstructural properties of the resulting coating[27].

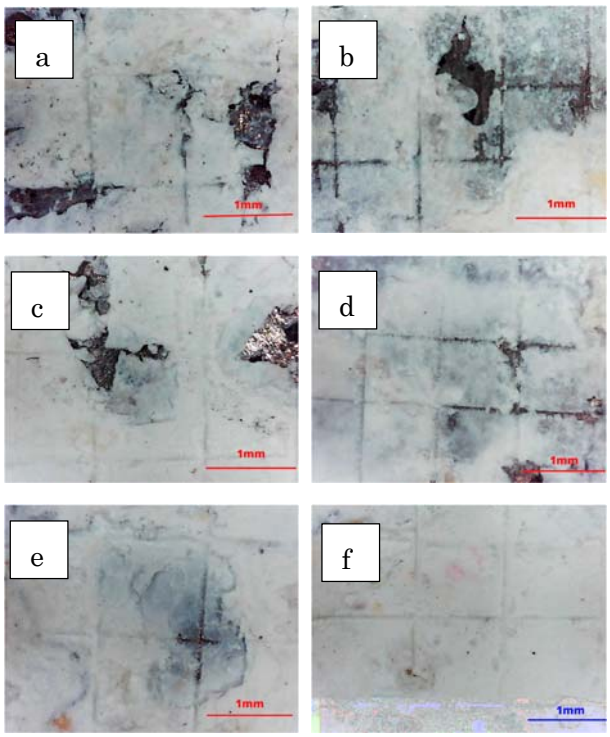

Fig 5: Photograph of Hydroxyapatite/Chitosan coating after Adhesive test, a) 5 V-10 minutes, b) 5 V-15 Minutes, c) 6 V-10 minutes, d) 6 V-15 minutes, e) 7 V-10 minutes, and f) 7 V-15 minutes

Table 4. Result of The Adhesive Test

Specimen Codes	Classification (ISO 2409)
5 V - 10 min	3
5 V - 15 min	2
6 V - 10 min	2
6 V - 15 min	1
7 V - 15 min	0
7 V- 15 min	0

4. Conclusions

Based on this study, the applied voltage and the electrophoretic deposition time influenced the resulted coating properties of HA/CS composite on the porous titanium. The higher voltage is in line with the higher deposit weight of the HA/CS composite on the porous titanium substrates. Furthermore, the longer time will also increase the deposit weight of HA/CS coating on porous titanium. Optimizing the applied voltage and the electrodeposition time will increase the coating thickness and increasing the adhesive strength. It was shown in this study that the adhesive quality of the coating on the substrate increased as the voltage and electrophoretic time increased. 7 V-10 minutes and 7 V-15 minutes are shown to be the optimum electrophoretic deposition parameters due to large HA/CS deposits, pores coverage, homogeneity, and having the best adhesive test results.

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