



ELECTROPHORETIC DEPOSITION OF Ti6Al4V HYDROXYAPATITE COATING: ELECTRODE DISTANCE AND OPERATING TIME CHANGES

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ABSTRACT

The electrophoretic deposition (EPD) method is widely used to obtain a fine, uniform, and cost-effective hydroxyapatite (HA) coating on a complex-geometry substrate. This method was used in this study to coat Ti6Al4V with hydroxyapatite powder at different electrode distances and times. In this case, the electrode distance influenced the deposition current during the coating process, and decreasing the electrode distance resulted in more deposited hydroxyapatite. XRD analysis confirmed the generation of crystalline HA phase and vaterite during the EPD process. Optical microscopy revealed on the coated sample that the porosity was still interconnected, with pore sizes ranging from several microns. The electrophoretic coating had a time limit before the deposition became ineffective due to the low deposition current. In the future, the findings could provide a good strategy for preparing metal-based medical implants coated with hydroxyapatite research.

Keywords: coating, current density, electrophoretic deposition, hydroxyapatite, vaterite.

INTRODUCTION

Because of its bioactivity and osteoconductivity, as well as its potential for use in medical engineering such as scaffolds for bone grafting, hydroxyapatite (HA) is an attractive biomaterial. However, when it comes to producing complex designs with regulated microstructures, this type of ceramic has limitations (Sarkar and Nicholson 1996). As a result, for component strengthening and densification, the HA powder must be sintered at a relatively high temperature. In contrast, high-temperature sintering may cause the desired HA structure to disintegrate, compromising the material's biocompatibility (Van der Biest and Vandeperre, 1997). Hence, fine-grained powders are required to improve the scaffold's sintering performance at lower temperatures. As a result, a suitable fabrication strategy is required to provide the controlled aggregates of fine grains in order to generate the appropriate scaffold. Furthermore, the porous materials generated can be produced using a salt leaching and microsphere burnout method. These processes, on the other hand, frequently use the additive/binder strategy, which have limitations in terms of completing the removal of the additives/binders as well as minimal bonding strength. In this case, electrophoretic deposition (EPD) technology offers a simple way to increase the porosity of the biomaterial.

EPD provides a reasonable coating method for varying biomaterials for this purpose due to its ease of use and low cost (Boccaccini and Zhitomirsky, 2002; Corni *et al.*, 2008; Boccaccini *et al.*, 2010). Surface coating on metallic bone implant materials could be one of the intriguing possibilities. The use of biocompatible calcium orthophosphate (Ca-P) coating on biomaterial implant material increases bioactivity while decreasing potentially harmful metal ion leakage (Narayanan *et al.*, 2008;

Cadosch *et al.*, 2009; Addison *et al.*, 2012). Plasma spraying deposition, electrostatic spray deposition, and pulsed laser deposition are some other Ca-P coating processes used in industry (Combes and Rey, 2010). EPD, on the other hand, has a significant advantage over previously described approaches in that it can cover the inside of porous materials and operates at room temperature (e.g. Tissue scaffolds).

EPD is also one of the most effective and efficient small particle assembly technologies (Boccaccini and Zhitomirsky, 2002; Corni *et al.*, 2008; Boccaccini *et al.*, 2010). This technique has grown in popularity due to its ease of use, low equipment costs, and ability to create elaborate structures and patterns. There has recently been a surge of interest in its biological applications (Basu *et al.*, 2001; Chávez-Valdez *et al.*, 2012). Because previous research has primarily focused on the fabrication of thin HA coatings on metals or ceramics, the use of EPD to manufacture bulk HA scaffolds has the potential to be one of the most cost-effective forming techniques for complex structures. However, it has been suggested that depositing a thick HA coating with the required porosity and bioactivity is extremely difficult. As a result, intensive work on the EPD method for HA coating, as well as a thorough understanding of surface chemistry and physics, is required.

In the present study, the hydroxyapatite (HA) powder was deposited on titanium-alloy (Ti6Al4V) plates using the direct current-EPD (DC-EPD) method with ethanol as the suspending medium. Because it is stable enough for the HA suspension during the EPD process, ethanol was chosen. The coated sample was sintered after the HA powder was deposited to ensure adequate adherence to the substrate. To confirm the formation of the HA phase, the following X-ray diffraction (XRD) and



optical microscopy analyses were performed on the surface of the coated samples. Surface response methodology (SRM) was used to optimize EPD parameters (time, deposition current, and electrode distance) to provide the best yield of deposition flux and coating mass. The findings of the study were expected to provide the appropriate parameters for producing the thick HA deposit with the desired porosity.

METHODOLOGY

Materials

Ti6Al4V plates (1 mm thick) cut to 25x10 mm substrates were used as working and counter-electrodes. These substrates were agitated in an ultrasonic bath (Fischer Bioblock Scientific) with ethanol, and high purity water for 15 minutes each. After cleaning the plates and immersing them in pure ethanol (C₂H₅OH), they were ready for use. A 2g/L HA suspension solution was created by combining 0.5 g HA (Merck, Analytical grade > 90%) with 250 mL ethanol (C₂H₅OH) and 3 molar HNO₃ until the pH reached 3. Prior to deposition, the suspension was agitated for 60 minutes at 200 rpm using a magnetic stirrer.

Electrophoretic Deposition

The purpose of the EPD experiment was to see how electrode distance and deposition time affected the resulting HA coating mass. The colloid was prepared for the EPD process with an adjusted pH value of 3.0 at a constant voltage of 30 V, a solution temperature of 50 °C, and a stirring speed of 150 rpm. In the EPD cell, the cathodic electrode was a graphite plate, and the counter electrode was Ti6Al4V. The distances between the cathode and anode were 10, 15, and 20 mm, respectively, and the deposition area was 2.5 cm². For operating times of 3, 5, and 7 minutes, single deposition to the desired thickness was performed. After that, the coated samples were air dried for 24 hours.

Surface Characterisation

Surface samples were subjected to an X-ray diffractometer (XRD 6000, Shimadzu, Japan) for XRD data collection, which was compared to the XRD of the substrate Ti6Al4V plates. In addition, for qualitative analysis of the synthesized product, a QualX search-match program was used to verify the phases generated from the APD process (Altomare *et al.*, 2008). The surface morphology and cross-sections of the coated samples were examined using an optical microscope (Olympus, BX53M). By multiplying the difference between uncoated and coated mass by 100 percent, the percentage of coating mass was calculated.

Conceptualization of the SRM Model

The SRM model was approached through the use of two quadratic polynomial equations (Eq. 1) that relate the response of yield HA mass coatings versus EPD parameters. The polynomial equations were resolved separately based on two responses to determine the relationships and interactions between the responses and the deposition parameters.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j}^{\infty} \beta_{ij} x_i x_j + \epsilon \quad (1)$$

where Y denotes the dependent variable, β_0 denotes the constant coefficient, X_i denotes the i th independent variable, and X_j denotes the j th independent variable. Electrode distance and time are the independent variables X_1 , and X_2 , respectively. The linear effect is denoted by β_i , and the squared effect is denoted by β_{ii} , while β_{ij} denotes the interaction effect of the variables X_i and X_j .

RESULTS AND DISCUSSIONS

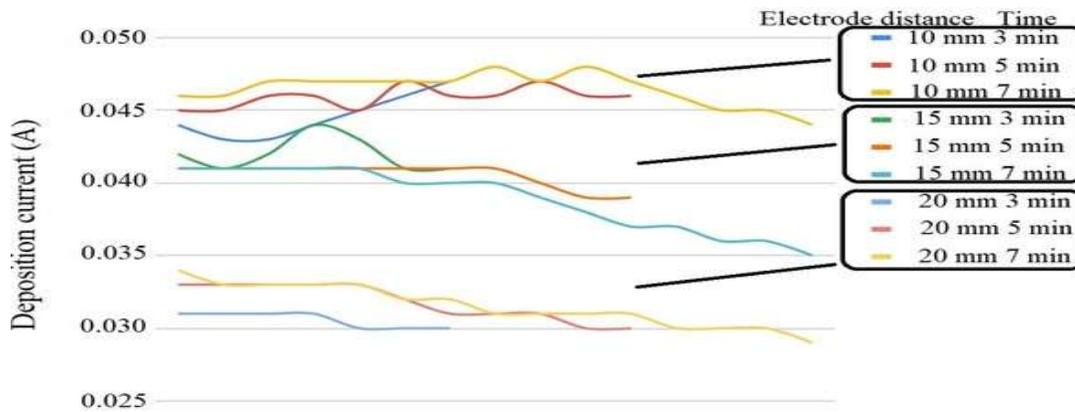
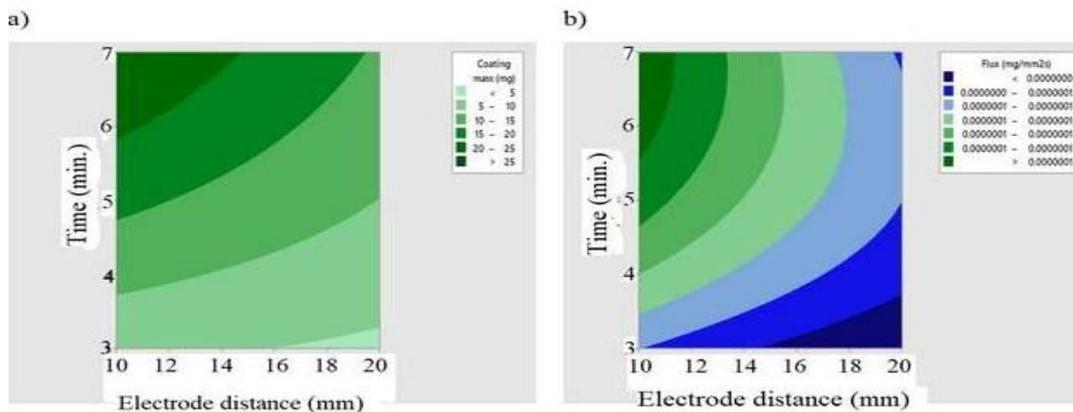
Deposition Rate and Coated HA Mass

The actual values of the deposition yield model's response are shown in Table-1. As the electrode distance increased up to 20 mm, the deposition yield appeared to increase. The deposition mass rate appeared to decrease with increased or prolonged operating time at a constant voltage (Basu *et al.*, 2001). This is consistent in constant voltage EPD because, while the potential difference between the electrodes remained constant, the electric field influencing electrophoresis decreased with deposition time due to the formation of an insulating layer of HA particles on the electrode surface (Basu *et al.*, 2001). During the early stages of EPD, however, the deposition mass and time have a generally linear relationship. The findings were very consistent with previously published data (Besra and Liu, 2007). As a result, as the deposit grew over time, the available electrical current of suspension fluctuated and decreased, whereas increased deposition rate required less deposition current with increased electrode distance (Figure-1).

Correspondingly, the optimization of the EPD parameters was made by SRM to achieve the desired HA coating deposition yield. Figure-2a depicts the 2D-response surface plots for the interaction influence of electrode distance (A) and operating time (B) on deposition mass yield. According to the contour plots, a longer coating duration time and a larger electrode distance result in a coating with a high mass. Furthermore, the deposition rate followed the same pattern as the yield mass response (Figure-2b). Under the described constraints, the optimum conditions for the maximum possible coated mass (> 25 mg) were found to be an electrode distance range of 10-14 mm, corresponding to operating time of 7 minutes, and a voltage of 30 V.

**Table-1.** EPD process experimental conditions for mass deposition.

Run	Parameters (Electrode distance and time)	Uncoated mass (mg)	Coated Mass (mg)	Δ mass (mg)	%	Deposition rate [mg/ (mm ² min)]
1	10 mm and 3 min	1043.1	1048.9	5.8	0.56	5.65×10^{-8}
2	10 mm and 5 min	1040.4	1058.4	18.0	1.73	1.06×10^{-7}
3	10 mm and 7 min	1043.8	1067.6	23.8	2.28	1.00×10^{-7}
4	15 mm and 3 min	1043.6	1048.7	5.1	0.49	4.93×10^{-8}
5	15 mm and 5 min	1044.0	1055.6	11.6	1.11	6.83×10^{-8}
6	15 mm and 7 min	1041.4	1062.8	21.4	2.05	8.94×10^{-8}
7	20 mm and 3 min	1043.8	1048.4	4.6	0.44	4.39×10^{-8}
8	20 mm and 5 min	1046.7	1056.5	9.8	0.94	5.66×10^{-8}
9	20 mm and 7 min	1043.2	1057.3	14.1	1.35	5.84×10^{-8}

**Figure-1.** Deposition current used to change the distance between electrodes and the operating time.**Figure-2.** Response surface demonstrating the effect of electrode distance and time on a) coating mass yield; b) mass deposition rate.

The Microstructure of the HA-Coated Product

The XRD results, shown in Figure-3, confirmed the presence of coated HA and vaterite (CaCO_3) in the surface layer of the Ti6Al4V substrate, where the XRD

peaks of Ti6Al4V could still be seen due to its porous nature. The current study suggested that metastable polymorphs of calcium carbonate (vaterite) formed because of the reaction of Ca^{2+} and CO_3^{2-} producing



CaCO₃ in ethanol, and sparingly reaction with PO₄³⁻ to form HA, as applied fixed voltage and varying operating times. Additionally, a cross-section of the generating coated mass from an optical microscope image analysis as shown in Figure-4 reveals that the pores are interconnected, while the pore morphology in the porous-coated HA has pores ranging in size from a few microns. As a result, EPD is a viable method for producing coated HA material with interconnected porosity and the desired thick coating. The current study aimed to demonstrate that proper control of the applied voltage causes particle movement, resulting in the desired deposit microstructure. In fact, as illustrated in Figure-4, the current porous matrix still has small pore sizes, i.e., micropores with diameters of about 1 μm. Further work at varying voltages should be done here to increase the thickness of the coating product.

Additionally, more cell culture experiments are needed to determine how well the obtained porous EPD

HA coating that can be applied to scaffold mimicked tissue formation in vivo on the 3D matrix, where the interrelated ceramic matrix pores may provide cell infiltration and aid in the formation of mature tissues (Ma *et al.*, 2003). On the other hand, a homogeneous porous scaffold with a 100 μm pore size may provide high-density cell cultivation (Tachibana *et al.*, 2002). A pore size of 300-500 μm may also be sufficient for rapid cell growth (Wintermantel *et al.*, 1996 and Tsuruga *et al.*, 1997). As a result, pores that are larger than the current resulting diameter may be designed to allow for adequate nutrient transport. This is due to the fact that the porosity structure and bioactivity of HA play a role in cell growth to some extent. Despite having unfavorable pore sizes for cell growth, this microporous matrix is critical for providing the overall matrix's bonding and structural strength. This particular property could be critical to fit into bone grafts.

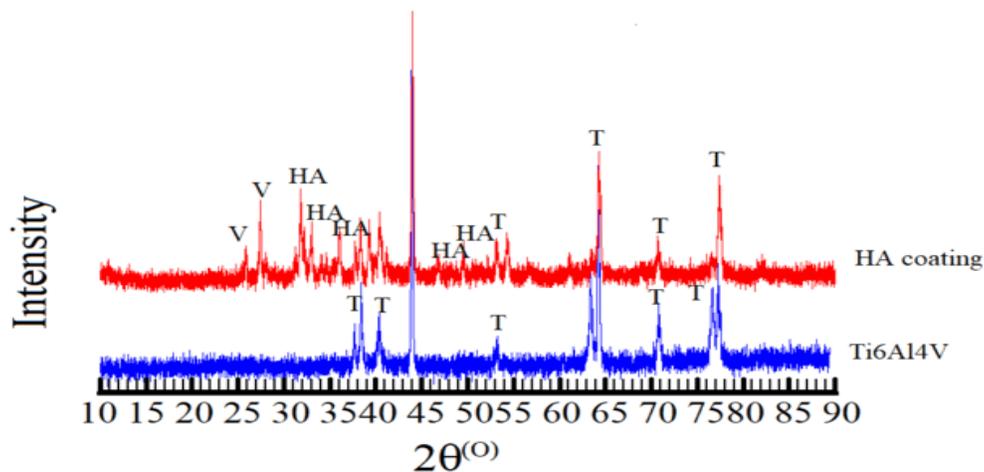


Figure-3. XRD patterns of the coated HA on the Ti6Al4V substrate (T), HA and V stand for hydroxyapatite and vaterite, respectively.

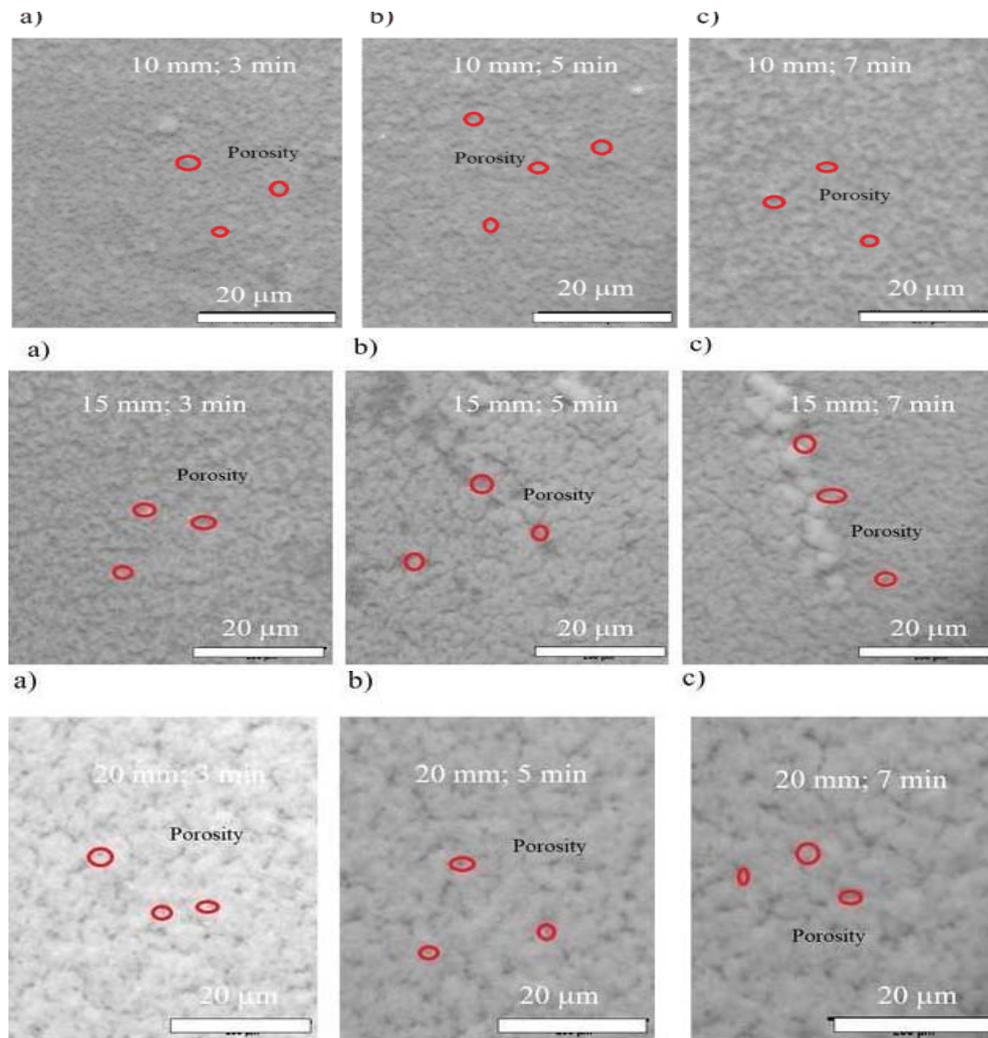


Figure-4. Optical micrographs of coated HA material demonstrating pore interconnectivity based on electrode distance and time; a) 10 mm at 3-7 min; b) 15 mm at 3-7 min; and c) 20 mm at 3-7 min.

CONCLUSIONS

The EPD of HA powders deposited on Ti6Al4V metallic implants produced a bulk porous HA product with uniform and crack-free interconnected porosity. A repeated deposition EPD procedure should be used to improve thick deposition. The ethanol-dissolved HA particle suspension was prepared, and the best deposition condition (pH of 3) were discovered at electrode distances of 10-14 mm and a 7-minute operating time. The XRD results confirmed the formation of the HA phase and vaterite during the EPD process. Optical examination revealed that the pores were interconnected and had pore sizes of about 1 micron. The EPD method simplified the process of coating HA on Ti6Al4V base metal. A cell culture experiment, however, is suggested to investigate the effect of bioactivity on pore interconnectivity and pore size.

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