Hydroxyapatite coating by electrophoretic deposition at dynamic voltage

Xianwei MENG\(^{1,3}\), Tae-Yub KWON\(^{1,2}\) and Kyo-Han KIM\(^{1,2}\)

\(^{1}\)Institute for Biomaterials Research and Development, Kyungpook National University, Daegu, Korea
\(^{2}\)Department of Dental Biomaterials, College of Dentistry, Kyungpook National University, Daegu, Korea
\(^{3}\)Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China

Corresponding author, Kyo-Han KIM; E-mail: kyohan@knu.ac.kr

The aim of this study was to evaluate hydroxyapatite (HA) coatings produced by dynamic voltage during electrophoretic deposition (EPD). Dynamic voltages from 0 to 200 V were incrementally applied in three interims. The as-deposited coating was sintered at 800°C and its properties evaluated. Structure and phase analyses of both as-deposited and sintered coatings were evaluated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The HA coatings obtained by dynamic voltage consisted of two layers. While the inner layer was dense and firmly attached to the substrate and contained fine HA particles, the outer layer was porous and contained bigger particles. Deposition was applied to increase the thickness of the coatings. SEM analysis showed that these coatings were free of cracks. In addition, decomposition of HA coatings was not observed until 800°C.

Key words: Hydroxyapatite coating, Electrophoretic deposition, Dynamic voltage

INTRODUCTION

Study of hydroxyapatite (HA) coatings on metal implants has been a subject of great interest in the area of biomaterials research for a long time and has drawn increasing attention, especially in the past decade\(^{1-4}\). Bioactive HA is deposited on surfaces of metallic implants to promote bone formation and enhance implant-bone adhesion. While bone compatibility is provided by the HA coating, the underlying metal possesses good ductility and strength. Deposition of HA coatings has been achieved by a number of methods, including plasma spraying\(^{5,7}\), ion implantation\(^{8,9}\), sputtering\(^{10,12}\), sol-gel coating\(^{13,15}\), biomimetic methods\(^{16-18}\), and electrophoretic deposition (EPD)\(^{19,21}\). Among these methods, EPD is a fairly rapid and inexpensive way of producing a dense and uniform coating on substrates even with complex geometries.

EPD is an old but effective technique for depositing on an electrode charge-carrying particles from a stable colloidal suspension, when under the influence of an applied direct current\(^{22-27}\). This method comprises two steps: the migration of charged particles in a liquid solvent by the action of an applied electric field (electrophoresis), and the coagulation of particles to form an adherent layer on the electrode (deposition). Coatings produced by this method are known for controlled thickness and morphology. Nonetheless, despite the huge amount of research effort on EPD processes, reports on the EPD of HA as the depositing material on titanium substrates are relatively limited\(^{28}\).

During deposition, one of the most important parameters is the electric field, which is applied either through constant current density or constant voltage across the electrodes in the suspension\(^{29}\). Most EPD processes are carried out under constant voltage conditions. Under low voltages (<20 V), small HA particles are deposited\(^{29}\). Application of higher voltages (>200 V) for periods longer than 10 seconds is reported to deposit bigger HA particles\(^{30}\). Increasing the electric field resulted in increased rate of deposition, but the deposited particles had shorter time to rearrange and therefore these coatings had a more porous microstructure\(^{30}\).

Previously, we reported that HA coatings prepared at dynamic voltages consisted of particles with continuous gradient, and that the morphology was distinctly different from that prepared at a constant voltage\(^{29}\). However, the dynamic process and deposition mechanism were not discussed clearly. In this paper, the dynamic deposition was intensely researched.

MATERIALS AND METHODS

Materials
Reagent grade HA powder (Yakuri Pure Chemical Co. Ltd., Japan) of 95% purity was used in this study. Morphology of starting HA powder particles had a needle-like shape, of which the diameters ranged 25–40 nm and length was about 150 nm. These powder particles were observed to have a typical HA crystalline structure.
Methods
1. Suspension preparation
In this study, the suspension for EDP consisted of ultrasonically agitated, ethanol-soaked HA powder. The HA concentrations in suspensions were 0.1% and 0.5%. Polyvinyl alcohol (3%) and N,N-dimethylformamide (DMF) (10%) were added to the suspensions to increase the adhesion of the deposited coatings and strength of the deposited material, as well as to prevent cracking.

2. Electrophoretic deposition
A glass cell of 1000 cm³ equipped with two platinum counter electrodes was used for electrophoretic deposition. Working area of the electrodes was approximately 3 cm², and separation distance between the working electrode and counter electrode was 3 cm.

During EDP, the suspension was adjusted to pH 4.0 and the process was carried out at either dynamic voltage or constant voltage in the range of 0–200 V from a power supply (HBPS-1A600V, Hobang Electronics Co. Ltd., Korea). Dynamic voltages from 0 to 200 V were incrementally applied in three interims. Primary voltage in the range of 0 to 10 V was applied at a rate of 0.0333 V/s. This was followed by a voltage between 10 to 50 V at a rate of 0.1 V/s, with final voltage between 50 to 200 V applied at a rate of 1 V/s.

The as-deposited coating was then dried in air for at least 24 hours. Sintering of the coating was done at 800°C for two hours at a heating rate of 10°C/min in argon atmosphere. SEM was used to analyze the microstructure of the as-deposited and sintered HA coatings, while XRD was used to analyze the phase compositions of HA powder and HA-coated specimen.

RESULTS
Figure 1 shows the representative surface morphologies of coatings deposited from bath having HA concentration of 0.1%. As shown in Fig. 1a, coatings deposited at 10 V contained fine particles, with few big particles sprinkled on the surface. In addition, the titanium substrate was partially coated with HA at 10 V, exhibiting a thin coating (Fig. 1b). When the applied potential was increased to 20 V, a thicker and more porous coating was observed (Fig. 1c). At an applied voltage of 200 V for three minutes, the coating surface was observed to be roughened and made up of larger agglomerated particles (Fig. 1d).

Figure 2 shows the surface morphologies of the coating prepared by dynamic voltage. As shown in Figs. 2a–2c, the coating layer closest to the substrate was observed to be composed of fine particles while the outer coating layers were composed of bigger particles.

The mass of each coating was measured by weighing, whereby the difference in specimen mass before and after EPD was the mass of the deposit. To compare the surface morphologies of coatings deposited by the constant and dynamic voltage methods, it was necessary to ensure that the HA coatings had approximately similar mass values. The deposit mass values of HA coatings after two, three, and four repeated dynamic voltage processes.
Fig. 2  Surface morphologies of the coating prepared by dynamic voltage: (a) is the final coating, (b) is the intermediate coating after the first step, (c) is the intermediate coating after the second step.

Fig. 3  Surface morphologies of HA coatings with similar deposit mass values prepared by repeated dynamic voltage at 0.1% HA concentration: (a) two depositions, (b) three depositions, and (c) four depositions. Deposit mass values were 0.0031, 0.0061, and 0.0078g respectively.

Surface morphologies of HA coatings obtained at a constant voltage of 10 V at 0.5% HA concentration after: (a1) 2 min, (b1) 5 min, and (c1) 7 min. Deposit mass values were 0.0031, 0.0055, and 0.0080g respectively.
were 0.0031, 0.0061, and 0.0078g respectively. By modifying the deposition conditions of the constant voltage process, approximately similar deposit mass values were obtained. The deposit mass values of HA coatings at 10 V after 2, 5, and 7 minutes of deposition at 0.5% HA concentration were 0.0031, 0.0055, and 0.0080g respectively. From Fig. 3, it could be seen that all the coatings produced using the repeated dynamic deposition process were dense, crack-free, and uniform. However, under constant voltage (10 V) and at a high HA concentration (0.5%), cracks in the coatings were observed (Fig. 3a1, b1, c1). Increasing the applied constant voltage (20 V, 200 V) increased the severity of the cracks (pictures not shown).

Figure 4 shows the representative SEM micrographs of coatings sintered at 800°C. The coatings displayed a polycrystalline HA microstructure and were free of cracks. However, many interconnected micropores were also observed within this structure. As shown in Fig. 5, X-ray diffraction patterns of the HA powder and HA coating sintered at 800°C showed well-defined peaks of HA structure.

**DISCUSSION**

Electrophoretic deposition is achieved by the motion of charged particles toward an electrode under an applied electric field. As such, coatings produced using EPD is governed by electrical parameters as well as the properties of the suspension.

During EPD, the electrophoretic velocity \( \nu \) of the charged particles can be described by the following equation:

\[
\nu = \frac{Q E}{4 \pi r \eta}
\]

where \( Q, r, \eta, \) and \( E \) represent the charge, particle radius, viscosity of the suspension, and the potential difference applied to the suspension respectively.

In suspensions with low solid concentration, \( \eta \) is often considered constant. Under this condition, the electrophoretic velocity is mainly a function of the electric field and the particle size. When \( E \) is constant, the suspension used for EPD usually has a distribution of particle sizes, and particles with different \( Q/r \) ratios have different electrophoretic mobility, thereby resulting in segregation during the EPD process. In addition, in a suspension of particles with different radii, preferential deposition of fine particles is expected because of their increased mobility compared to that of larger particles. Mobility of particles can also be improved by increasing the applied potential. This condition enables larger particles to be deposited besides finer particles. These theories help to explain the phenomenon observed in this study, substantiating the production of a porous and roughened coating at a higher electric field and the production of a dense coating of fine particles at a lower electric field.

The HA powder used in this study was of commercial grade and contained many agglomerated particles. It was difficult to control the particle size...
to a narrow size range, which meant that use of these powder particles would affect coating integrity. By applying dynamic voltage during EPD, it was observed that coatings with continuous gradient could be produced. The coating layer closest to the substrate was observed to be dense, whereas the outer coating layers porous. The production of dense coatings with initial voltage from 0 to 10 V suggested that only fine particles had enough speed to arrive at the cathodic titanium substrate. During the dynamic process, the electrophoretic velocity ($v$) in Equation (1) takes the following form:

$$d_s = \frac{Q}{4\pi \eta} \times d_e$$  \hspace{1cm} (2)

where $E$ is a variable during the application of dynamic voltage. Since $E$ is time-dependent [$E = f(t)$], the electrophoretic velocity ($v$) for the dynamic process can be described by the following equation:

$$v = \int \frac{Q}{4\pi \eta} \times d_e$$  \hspace{1cm} (3)

As such, the electrophoretic velocity during the dynamic process was a function of time and particle size. From Equation (1), it was shown that particles with the same size were deposited simultaneously under constant voltage, resulting in a layer of predominantly mono-sized particles. Equation (3) showed that under dynamic voltage, fine particles were deposited first. With increasing time and voltage, the larger particles acquired enough mobility and were deposited. This condition resulted in a coating gradient with increasing particle size. Mass of the coating produced using dynamic voltage was low. With repeated depositions, mass value increased and became comparable with the mass values of coatings produced using constant voltage in this study. It was observed that the coatings produced using repeated dynamic deposition process were dense, crack-free, and uniform. However, under constant voltage and at high HA concentration, cracks were observed. These observations were in agreement with previous studies, where a thicker HA coating was produced under constant voltage condition with increasing deposition time and increasing HA concentration in the suspension. However, under high HA concentration and at a constant voltage condition, spalling of the coatings due to drying shrinkage was also observed. It was also shown that, during the formation of a thick HA coating, repeated depositions before heat treatment were critical to decrease the amount of cracks arising out of drying shrinkage.

Figure 6 shows a schematic representation of the gradient HA coating achieved by applying dynamic voltage. The layer directly adhering to the titanium substrate consisted of fine particles, where there was very little opportunity for large particles to be deposited as a result of low voltage. When voltage was increased, the coatings consisted of larger particles. It was also suggested that the uniform, densely packed layer of mono-sized particles achieved 64% of the theoretical density. However, it was probable that the layer containing particles of varied sizes produced a density as high as 73%. This was because the smaller particles filled up the gaps between the larger particles. In light of the findings in this study, dynamic voltage EPD soundly presented itself as a promising method to achieve dense coatings.

Sintering of the EPD coatings resulted in coatings exhibiting well-defined peaks of HA. In other words, the phase structure of HA coating produced was not compromised during sintering.

**CONCLUSIONS**

This study showed that dynamic voltage EPD was a valid technique for producing HA coatings with gradient structure. The use of dynamic voltage EPD resulted in a coating layer of dense HA adjacent to the titanium substrate and porous outer layers. Coating thickness and deposit mass could be controlled by repeated depositions without significant changes in coating morphology. Indeed, repeated
dynamic voltage EPD was able to produce a thick, uniform, and crack-free HA coating. In addition, sintering of the HA coatings at 800°C for two hours did not change the original structure.

REFERENCES