

## HYDROXYAPATITE COATING ON TITANIUM SUBSTRATE BY ELECTROPHORETIC DEPOSITION

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**ABSTRACT :** Several methods have been used to coat Hydroxyapatite (HA) on metal substrates such as plasma spraying, dip coating, vacuum coating and electrophoretic deposition (EPD). In this work, EPD method has been used to coat HA on titanium substrates. The deposition was conducted under applied voltages of 10, 20, 30, 40 and 50 V in colloidal suspension containing 2.5 and 5.0 wt. % HA in ethanol. Deposition at higher voltage produced higher volume mass of the coating. Coating consisting of bigger particles size was deposited at higher deposition voltage. After deposition, the coating was dried at room temperature followed by sintering at 900 °C in argon atmosphere to improve adhesion and density of the coating. The phase purity and morphology of the as-deposited and sintered coatings were analyzed by XRD and SEM. It was found that EPD method is capable of coating HA on titanium substrates and HA coating on titanium substrate retained its phase after sintering at 900 °C.

**KEYWORDS :** Hydroxyapatite, electrophoretic deposition, sintering, deposition potential

## INTRODUCTION

Hydroxyapatite (HA) has been widely used in medical and dental applications due to its close similarity in chemical composition and biocompatibility to natural tissue (Hench, 1998). However, poor mechanical properties of HA (fatigue properties in particular) leads to its limitation to be used in bulk form for load bearing application in orthopedics (Garcia-Sanz *et al.*, 1998). Titanium/titanium alloys and stainless steel are commonly used in bioimplants application and are proven to be potentially suitable for load bearing applications. Thus, the concept of coating implants surface with HA provides both the benefits of biocompatibility of HA and load bearing capability of the implants (Yildirim *et al.*, 2005). Many techniques have been used to deposit HA, such as plasma spraying, dip coating, vacuum coating and electrophoresis (Garcia-Sanz *et al.*, 1998; Mavis *et al.*, 2000). Plasma spraying is the most widely used for HA deposition. This process is however associated with high working temperature, which can lead to the decomposition and phase transformation of HA. Furthermore, this process is a line of sight process, which means it is not suitable for coating complex geometry substrates (Ma *et al.*, 2003). These problems can be addressed by using a technique that operates at low (room) temperature. One such process is electrophoretic deposition. Electrophoretic deposition offers some advantages over other techniques, such as low cost, simple setup and its ability to coat complex shape objects. In addition, by adjusting deposition parameters and conditions, various coating morphology and properties can be obtained (Wang *et al.*, 2005).

Electrophoretic deposition is quite a simple process (Figure 1). The mechanism of electrophoretic deposition involves two steps. In the first step an electric field is applied between two electrodes and charged particles suspended in a suitable liquid moved toward the oppositely charge electrode. In the second step, the particles accumulate at the deposition electrode and create a compact and homogenous film (coating). For deposition of HA, a colloidal suspension consisting of HA particles (less than 100 nm in sizes) are dispersed in ethanol. In this case, the substrate is placed in the suspension and the electric field (ranging from 10 to 50 V) is applied between the electrodes. Since the charge of the HA particles in ethanol is positive, HA coating will develop on negative electrodes. The coating is then sintered to produce a dense and compact coating. However, sintering process must be done at elevated temperature of 900 °C to avoid the decomposition of HA coating to tricalcium phosphate (TCP) because of the migration of metals ion into the HA.

## MATERIALS AND METHODS

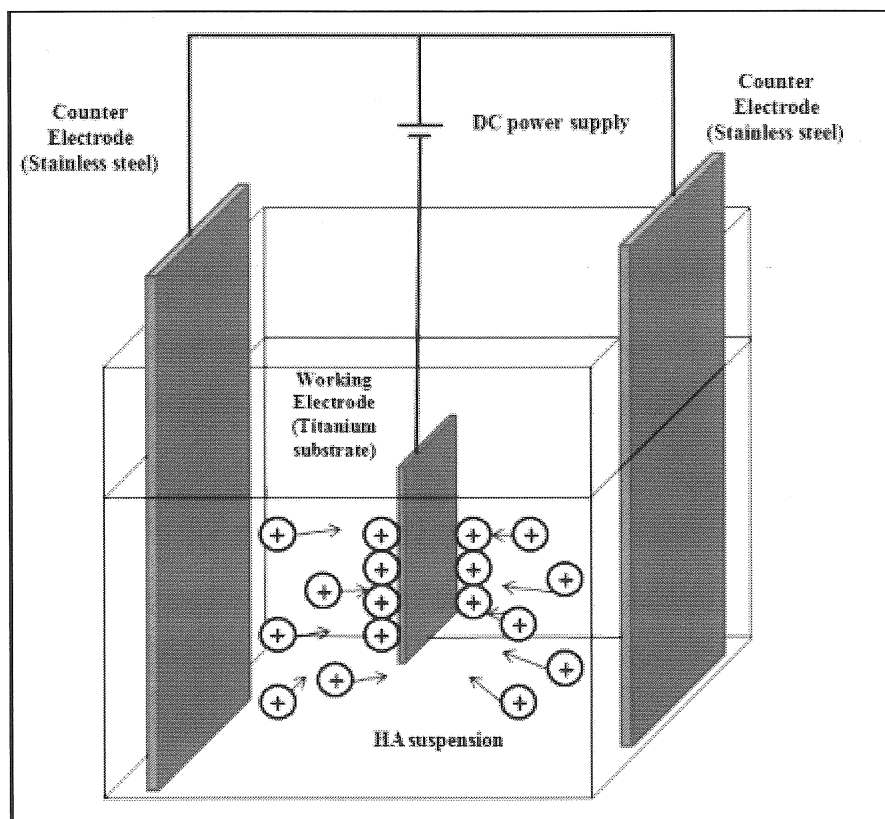
Titanium substrates with the dimension of 26 x 15 x 1 mm were used as substrate. Before deposition, pure titanium plates were ultrasonically cleaned with ethanol. The suspension was prepared by adding 2.5 g HA (1.25 wt. %) and the other suspension 5.0 g HA (2.50 wt. %)

in 250 ml ethanol. The suspension was then dispersed ultrasonically by VCX 750 ultrasonic processor for an hour.

The suspension was rested for 4 hours to eliminate the bigger particles by sedimentation. The deposition was performed with titanium plate as the working electrode (negative) and stainless steel foil as the counter electrode, under various potential at room temperature according to parameters listed in Table 1.

**Table 1.** Deposition parameters used to deposit HA

Deposition Time	5 minutes
Deposition Voltage	10, 20, 30, 40 and 50 V
Sintering Temperature	Room temperature, 900 and 1100 °C
Sintering Time	1 hour



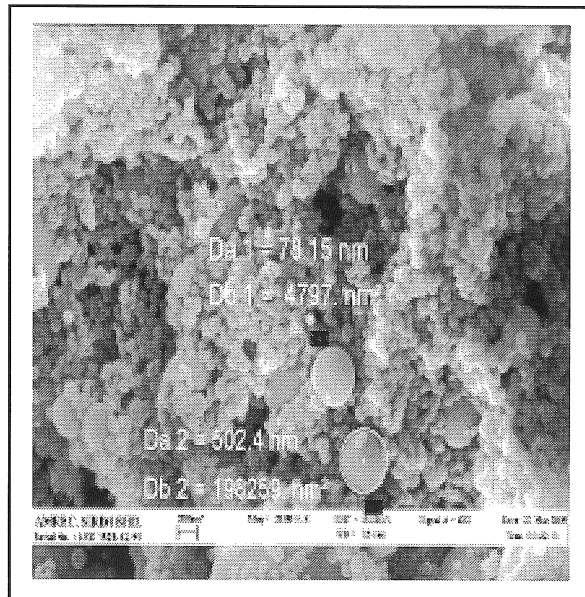
**Figure 1.** Schematic illustration of EPD process

After deposition, the surface morphology of the resultant HA coatings were observed under SEM using LEO 1525 FESEM. Composition of HA coatings were analyzed by XRD to identify the composition of HA before and after sintering. The equipment used for XRD analyses was Bruker XRD equipment with CuK X-ray source.

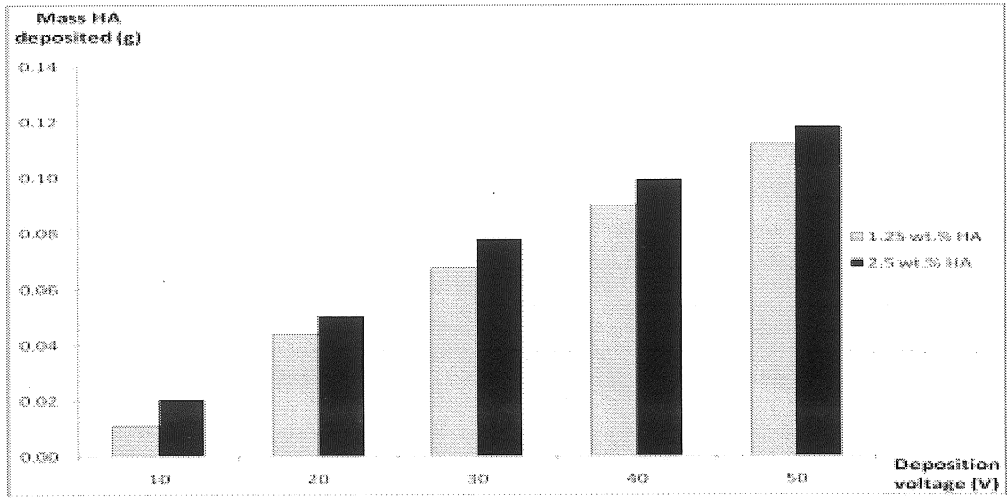
## RESULTS AND DISCUSSION

### Electrophoretic deposition

HA powder used in this work was commercial HA powder purchased from Sigma Aldrich with average particle size of less than 200 nm (manufacturer specification). The image of the powder is shown in Figure 2. Figure 3 depicts the mass of the coating deposited at different deposition voltages for the deposition time of 5 minutes each. It can be seen that increasing the deposition voltage would also increase the mass of the deposited HA coating. This trend was observed in both of the HA suspensions (1.25 g and 2.5 g). However, it is also observed that deposition from a highly concentrated suspension (2.5 g) would produce coating with higher mass as compared to lower concentrated suspension (1.25 g), while maintaining the same deposition voltage and duration. We also calculated the average coating or deposition speed by dividing the value of mass deposited with the deposition time, and the values and trend of the coating speed are shown in Table 2 and Figure 4 respectively. Generally, it can be said that higher deposition speed can be achieved by using higher deposition voltage.



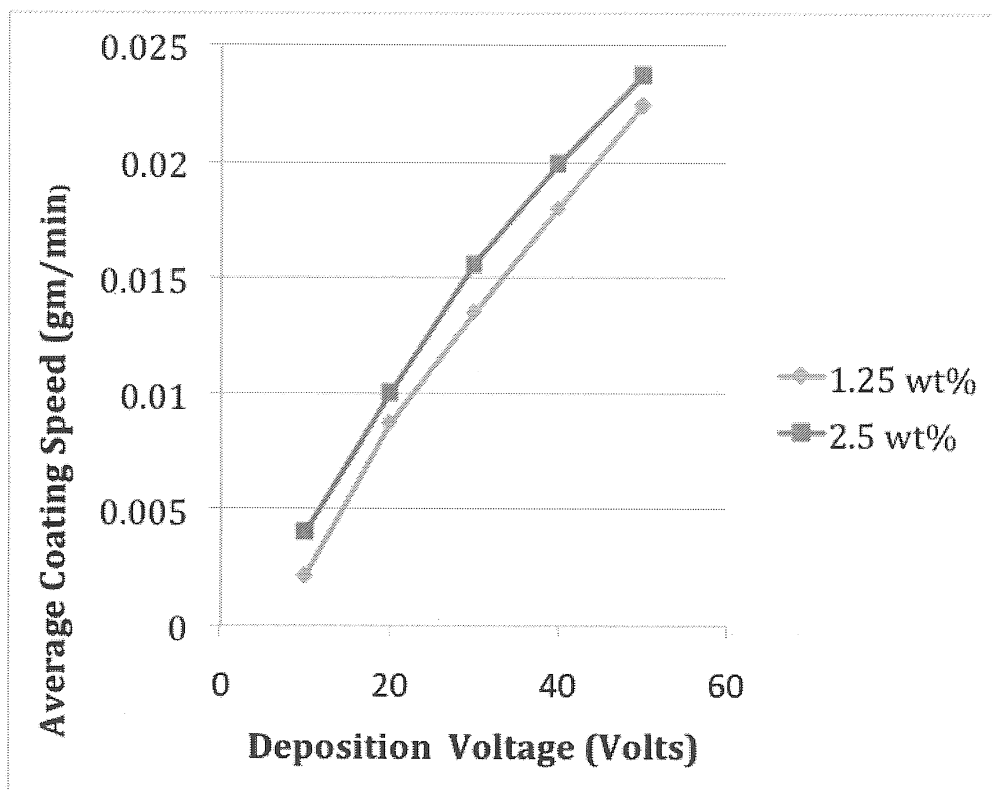
**Figure 2.** SEM image (20,000 x) of as received HA powder



**Figure 3.** Mass HA deposited at various applied voltages (10-50 V) in different suspension concentration of HA

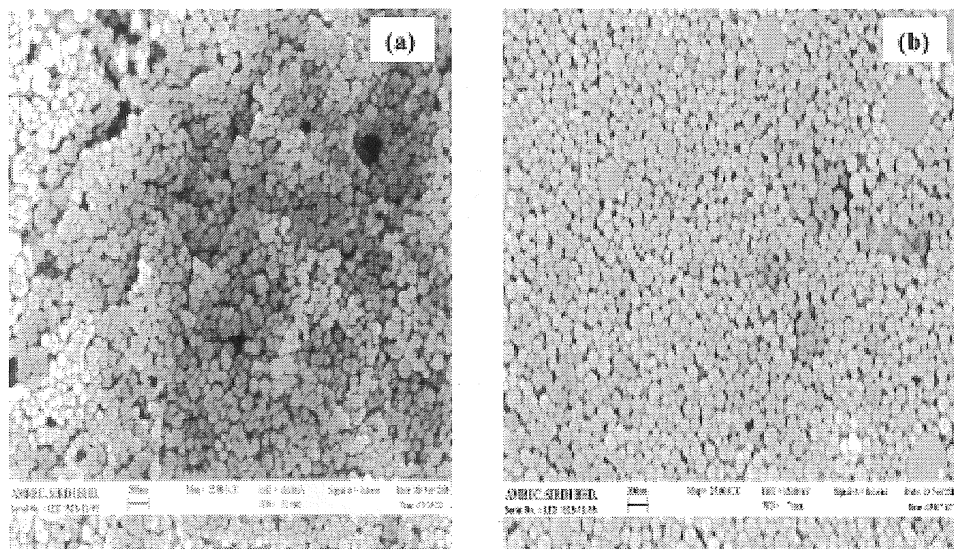
**Table 2.** Coating parameters at various deposition voltage

Deposition voltage (v)	Average coating speed in Suspension Concentration [1.25 %] (g/min)	Average coating speed in Suspension Concentration [2.5 %] (g/min)
10	0.00216	0.00406
20	0.00876	0.01006
30	0.0135	0.0156
40	0.018	0.01992
50	0.02242	0.02372



**Figure 4.** Mass HA deposited at various applied voltages (10-50 V) in two different suspension concentration of HA; deposition time: 5 minutes. Also shown are the values of average coating speed of HA particles (Table 2, Figure 4)

Figure 5 shows the surface morphology of coatings deposited at 10 V deposition voltages from suspension having HA concentration of 1.25 wt % and 2.5 wt % respectively. As shown in Figure 5, coatings mainly were formed from fine particles distributed uniformly on the substrate surface.

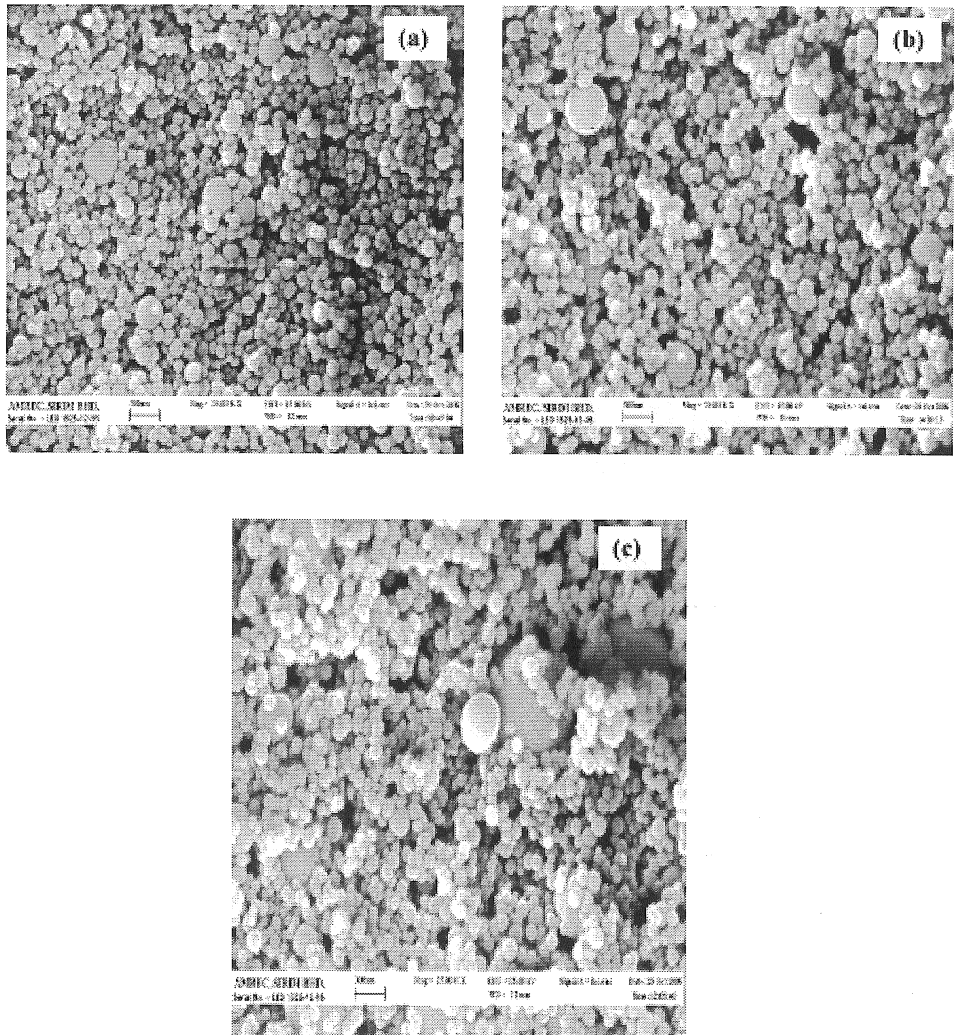


**Figure 5.** SEM image (25kx) of HA coating (a) 1.25 wt. % and (b) 2.5 wt. % of HA suspension deposited at 10 V applied voltage

In Figure 6, it can be seen that the HA particulates deposited at different deposition voltages. The coatings formed appear to be uniform, compact and fully cover the surfaces. Coating deposited at lower voltage seems to consist of smaller particles, while at higher deposition voltage we can observe that some of the larger particles were also deposited on the substrate. This can be explained by the equation related to the electrophoretic velocity ( $v$ ) represented by the following equation (1):

$$v = \frac{QE}{4\pi r \eta} \quad (1)$$

where  $Q$ ,  $r$ ,  $\eta$  and  $E$  represent the charge, particles' radius, viscosity of the suspension and the potential difference applied to the particle suspension respectively. The  $\eta$  can be considered constant because the concentration of the HA particles is relatively low.

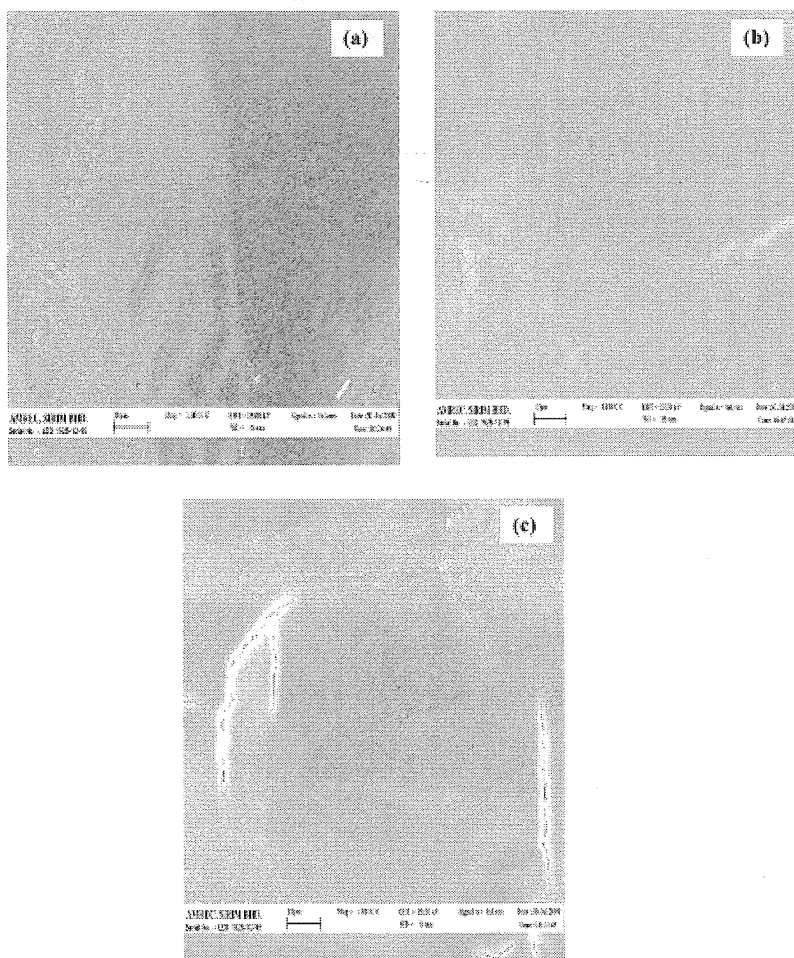


**Figure 6.** SEM image (25kx) of unsintered HA coating (1.25 wt. %) deposited for 5 minutes at different potential applied (a) 10 V (b) 20 V (c) 30 V

So, the electrophoretic velocity is mainly the function of the intensity of the electric field and the particle size. It can be seen that at lower voltage (smaller E), only the smaller particles can move fast enough to be deposited on the electrode, while the bigger particles were slow to move or unable to overcome the liquid/suspension resistance, hence no deposition of the bigger particles occurred. By increasing the deposition voltage, we can see that some of the bigger particles were deposited together with the smaller ones. It can be inferred that the voltage applied in the EPD influenced the selectivity of HA particles in the resultant coatings.



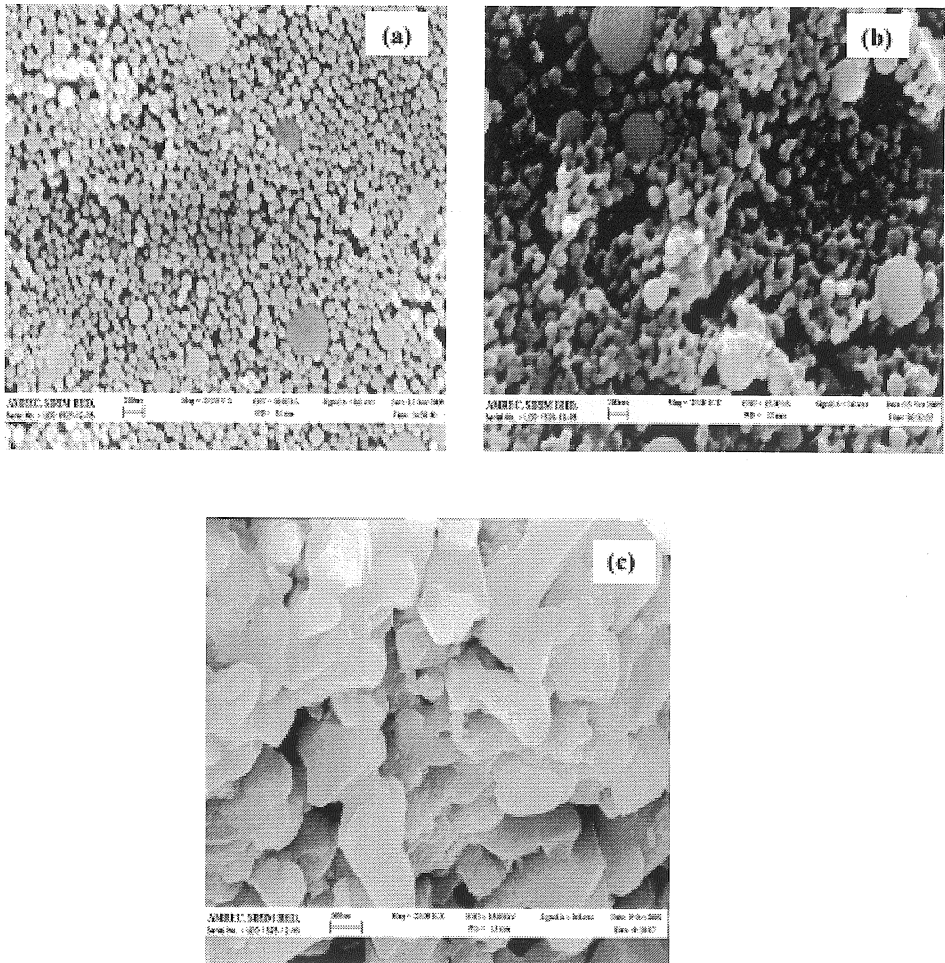
Figure 7 shows The EPD-formed coating layers obtained using suspensions with a constant HA loading of 1.25 wt. %, at the applied voltage of 10, 30 and 50 V dc respectively for the deposition time of 5 minutes. Under those parameters, increasing the deposition voltage provided a deposit with higher thickness as evident from the higher mass accumulated, as stated earlier. The deposition at higher voltage, in this case 50 V, produced coating with cracks on the substrate surface. During drying process, the volume of HA coating decreased due to rapid evaporation of ethanol which caused the surface stress and shrinkage to the coating. Because of the higher coating volume or thickness, coating deposited at high voltage is highly prone to cracking, due to the occurrence of more volumetric shrinkage. Consequently, there seem to be a trade-off between coating speed and quality of coating. In our experiment, we observed that coating deposited in the range of 10 to 30 V provided a good quality of coating and an acceptable coating speed.



**Figure 7.** SEM image (1 000x) of HA coating (1.25 wt. %) deposited for 5 minutes at various potential applied of; (a) 10 V (b) 30 V (c) 50 V before sintering

To investigate the sinterability of the HA coatings obtained, samples were electrophoretically coated at 20 V for the duration of 5 minutes, and were then sintered at 900 and 1100 °C. Figure 8 shows the SEM micrographs of coatings sintered at 900 °C, 1100 °C and a non sintered one. As-deposited substrate were analyzed by EDX before and after sintering to illustrate the appearance of calcium, and to determine if any elemental changes occurred on the sintered and the coating respectively. It was observed that there were no significant changes in elemental composition of the coating before and after sintering. However, the morphology of the coatings sintered at 900 and 1100 °C exhibited significant difference. At 900 °C we observed an incomplete bonding between particles, while at 1100 °C; the

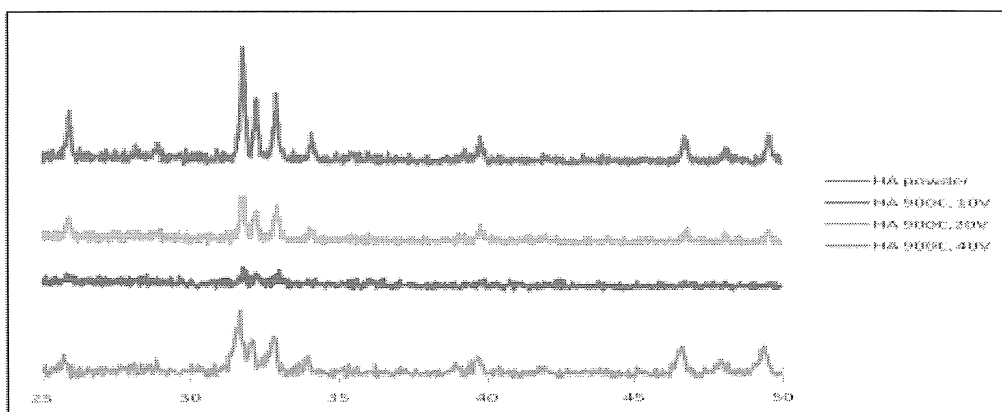
### 3.1 Sintering of coatings



**Figure 8.** SEM image (25kx) of HA coating (1.25 wt. %) deposited for 5 minutes at deposition potential of 20 V (a) before sintering and after sintering (b) 900 °C, (c) 1100 °C.

particles were transformed, probably because of the complete melting of HA particles. We anticipated that a workable sintering temperature is between those two temperatures, which can be determined experimentally.

Figure 9 shows the XRD patterns of HA coating at different voltage applied during HA deposition and sintered at 900 °C under Argon environment for an hour. Basically, we have the same composition and phase of the as received HA powders and coatings sintered at 900 °C. At 900 °C, the HA coating still retained its chemical composition and phase. The different peak intensities of HA in Figure 9 simply correspond to the different amount of HA present in the respective samples, i.e. deposition at higher voltage would produce coating with higher mass/thickness, hence the higher counts/intensities at respective peaks.



**Figure 9.** XRD patterns of HA powder and HA coating at different voltage applied during deposition (10 V, 20 V and 40 V) and sintered at 900 °C

## CONCLUSION

HA coating with various deposition voltage were successfully produced via the electrophoretic deposition method using commercial hydroxyapatite powder. The effects of sintering temperature, deposition voltage and HA concentration on the physical properties were studied. Sintering of the HA coating on titanium substrate did not alter the HA composition for the sample after sintering at 900 °C. The sintering process improves bonding between HA coating particles. The average particle size of HA deposited increased with the increased of the deposition voltage. Deposition at low deposition voltage (10 V) results in deposit coating of smaller particles. Whilst, deposition at higher voltage (50 V) result in deposit coating of smaller particles together with the larger ones. Both suspensions produced uniform coating, compact and fully covered the surfaces of the substrate. In this case, it was found that HA suspension with 2.5 wt. % was better as it promoted a higher coating speed. Deposition voltage between 10 and 30 V was found to be optimum as the coatings produced at these voltages were found to be uniform and free from cracks.

## ACKNOWLEDGEMENT

This work was supported in part by SIRIM Berhad and the Ministry of Science, Technology and Innovation, Malaysia (MOSTI) for financial support in this research work under Science Fund Grant No: 03-03-02-SF0096.

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