Micro-arc oxidation of bioceramic coatings containing eggshell-derived hydroxyapatite on titanium substrate

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\textbf{A B S T R A C T}

In the present study eggshells-derived hydroxyapatite (EHA) coatings were successfully produced on Ti6Al4V substrates using micro-arc oxidation process (MAO) at various concentrations of EHA (i.e. 1, 1.5 and 2 g/L) in an electrolyte consisting of tri-sodium orthophosphate. The attributes of the coatings were determined by X-ray diffraction, attenuated total reflectance-fourier transform infrared spectroscopy, field emission scanning electron microscopy and energy dispersive X-ray spectroscopy. The adhesion strength was evaluated using micro scratch tester, while the corrosion behavior of the MAO-coated substrates in phosphate buffer solution was determined by an electrochemical method. The results showed that as the EHA concentration increased, this was accompanied by a reduction in the porosity due to the formation of a dense and thick coating layer. This has also resulted in an increased in the surface roughness and degree of crystallinity of the HA phase. The MAO-coated substrate prepared with 1.5 g/L EHA concentration exhibited a well-formed coating layer with improved adhesive strength and excellent corrosion resistance. The mechanism of EHA-coating formation as well as the enhanced corrosion resistance of the coated substrates were discussed. This research shows the viability of using calcium-rich waste eggshells to produce phase pure HA suitable for coating on Ti6Al4V substrate using MAO method.

1. Introduction

There has been an increasing demand over the years in the development of a new generation of biomimetic implants to replace the dysfunctions of bones and natural tissues resulting from traumatic fracture, spine fusion, bone cysts, tumors or even due to aging [1]. A high percentage of implants are made of metallic biomaterials for the reconstruction of hard tissues and the most commonly used metallic biomaterials are stainless steels, cobalt (Co)-chromium (Cr) alloys, titanium (Ti) and its alloys. Ti-based materials are considered light in weight, biocompatible, highly corrosion resistance and possess high specific yield strength amongst metals [2,3]. However, the difference in mechanical properties (e.g. elastic modulus) between the natural bone and Ti-based metals result in undesirable effects such as poor osteoconductivity [4,5] as well as stress shielding [6] which may lead to re-fracture of the bone and loosening of the implant [7,8]. Generally, titanium and its alloys are bio inert, therefore, they cannot produce a chemical bond with the host tissue. In contrast, bioceramics exhibit surface reactivity that helps to develop good bonding with the bone and enhance tissue formation. During implantation, reactions occur at the interfaces between the implant surface and hard tissues which lead to time dependent changes on the surface characteristics of the implant material [9,10]. Hydroxyapatite (HA) is a widely researched bioceramic for use as a bone substitute material in orthopedics and dentistry mainly because of its chemical similarity to the mineral component of bones and hard tissues in mammals, as well as its extraordinary osteoconductive and osteointegrating characteristics [10,11]. Although, HA bioceramic has been applied extensively in medical applications,
this bioceramic cannot be employed as a monolithic implant for applications subjected to tensile stress cycles due to its inherent brittleness and poor fracture toughness [12,13].

In order to overcome the issues faced by HA and titanium alloys, several studies have focused on modifying the titanium implant surface topography (physical or chemical) including the development of various surface coating treatments incorporating HA bioceramics [14,15]. Coating titanium and its alloys with a thin layer of HA is envisioned as a synergistic solution which presents the advantage of combining the mechanical strength of Ti and its alloys and the excellent biological ability of HA bioceramic. Hydroxyapatite deposited implant surface is known to establish direct biochemical bonds to the bone, triggered by the adsorption of bone-growth mediating proteins at the biomaterials surface [16,17]. Numerous methods have been employed to fabricate HA coatings including plasma spraying [18], sol-gel method [19], electrochemical and electrophoretic deposition [20,21], pulse laser deposition [22] and sputter deposition [23]. However, most of the HA coatings produced using the aforementioned techniques exhibit some drawbacks such as poor adhesion strength, low crystallinity and requires high process temperatures. In addition, the relatively high temperature employed in these processes [24] may cause thermal decomposition of the HA phase to form tricalcium and tetracalcium phosphates as well as microcracking of the coating due to post-process shrinkage [20,25].

Among the techniques that have been applied for the production of HA coatings, micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO) or spark anodizing is considered one of the most promising techniques for surface treatment. It is a convenient and an effective technique to produce porous, rough and hard ceramic coatings on metals such Ti, Mg, Al, Ta and Zr and their alloys [26,27]. MAO process is based on anodic oxidation of the metals in an aqueous electrolyte solutions. The application of high voltages that exceed the growing oxide film dielectric breakdown voltage [28] promotes the initiation of sparks due to micro discharge plasma channels formation on the outer-most layer of the metal surface. The multiple concurrent plasma discharges result in a localized high pressure and high temperature on the metal surface. Therefore, the coatings that are formed are mainly consist of substrate metal oxides combine with the oxides containing the elements that are incorporated in the aqueous electrolyte solutions [29,30]. The oxide coatings formed on titanium and its alloys by MAO has a double layer structure comprised of outer porous layer and inner barrier layer. The inner barrier layer enhances the corrosion resistance of the implant materials, while the porous outer layer is useful for their biological performance [31]. High quality coatings with controlled crystallinity, morphology and thickness can be produced by MAO through the selection of appropriate deposition parameters such as composition and temperature of the electrolyte, voltage, current density, treatment time, etc. [32,33]. Among the mentioned parameters, electrolyte composition is a significant factor governing the coating properties. Modifying the electrolyte composition influences the MAO process due to the change of the electrolyte properties, i.e. pH value, conductivity and viscosity, which may affect the coating morphology and properties.

In recent years, many researchers focus on methods to enhance the biological and/or mechanical properties of HA coatings by either reinforcing or doping it with Mg [34], Fe [35], Si, Zr [36], Mn [37], Cu [38] and Ag [39] using MAO or PEO technique. However, little attention has been paid to the use of HA extracted from natural resources and biowastes such as eggshells, seaweeds and animal bones. Most of the HA produced from these bio-sources are considered to be deficient in calcium and contain traces of essential elements naturally present in their crystal structure such as Mg, Si, Na, K and Sr which very much resembles the human bones [40–42].

In this study, chicken eggshells-derived HA (EHA) coatings were successfully formed on Ti6Al4V substrate via a one-step MAO process containing tri-sodium orthophosphate (Na3P2O7·12H2O) based electrolyte solution. The microstructure, phase composition, morphology and elemental composition of MAO coatings produced at different concentrations of EHA particles were investigated. The bonding strength and electrochemical corrosion behavior of the MAO coatings produced with different concentrations of EHA were also examined.

2. Materials and methods

2.1. Synthesis process of EHA powder

In this research, waste chicken eggshells were washed with water thoroughly and dried prior to removing the inner membrane of the eggshells. The dried eggshells were ground into powder using a mortar and pestle before calcination at 900 °C at 10 °C min⁻¹ ramp rate (cooling and heating) for 1 h in order to transform the CaCO3 in the eggshells to CaO. The calcined CaO was mixed with distilled water to form Ca(OH)2 solution which acts as the calcium precursor. The derived Ca(OH)2 solution was then reacted with H3PO4 (85% purity, Merck) at a Ca(OH)2 to H3PO4 molar ratio of 1.67:1 [43]. In a typical synthesis process, the H3PO4 solution was added dropwise at a rate of 15–25 drops/min. into the calcium precursor under stirring condition at room temperature. In order to maintain the pH of the mixture above 10.5, ammonium hydroxide (NH4OH) (25% purity, Sigma-Aldrich) was added if required. After the reaction is completed, the product was allowed to settle for 24 h prior to filtering and washing with distilled water. Subsequently, the filtered cake was dried in an oven at 60 °C for 24 h, followed by crushing and sieving to obtain a soft and fine EHA powders.

2.2. Preparation of Ti6Al4V substrate

Rectangular samples (20 mm × 10 mm × 1.5 mm) of Ti6Al4V (Grade 5) alloy was used as substrate material in this study. The surface of the substrate was prepared by grinding successively using a rough (#400) to fine (#2000) SiC paper. The substrates were subsequently cleaned with acetone and distilled water sequentially in an ultrasonic bath for 20 min and finally dried under warm air.

2.3. Electrolyte preparation and MAO coating

In the present work, four suspensions were prepared by adding EHA with concentrations of 0 g/L (EHA-free), 1 g/L, 1.5 g/L and 2 g/L, subsequently designated as E0, E1, E1.5 and E2, respectively into 0.026 M of Na3PO4·12H2O solution. The suspensions were stirred for 30 min and dispersed in an ultrasonic bath for 2 h prior to the MAO treatment. The formation of the coating on Ti substrate was performed using a MAO set-up consisting of a DC power supply, stainless steel anode, graphite cathode and Ti substrate as the anode. The anodization treatment was performed with controlled cell voltage which was initially increased linearly to the target voltage and then maintained at the target voltage of 400 V for 10 min. The electrolyte temperature was maintained below 40 °C by adjusting the flow rate of the cooling water during the MAO process. These processing parameters were found to be the optimum which resulted in the development of a uniform thickness and well-defined coating morphology without delamination. After the MAO process, the coated specimens were cleaned with distilled water and dried with warm air.

2.4. Characterization of EHA and MAO coatings

The phases present in the synthesized EHA powder and MAO coatings were determined by X-Ray Diffraction (XRD) (PANalytical-Netherlands) operated at 45 kV/40 mA using Cu-Kα radiation source (λ = 1.5406 Å). The 2θ scanning range was 20°–80° at a step size of 0.02° and a scan speed of 1° min⁻¹. The structural changes and phase
composition were characterized by attenuated total reflectance using Fourier transform infrared spectroscopy (ATR-FTIR) (PerkinElmer FTIR, Spectrum 400). For each sample, 32 scans were recorded within a spectral range of 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. The surface morphology and the cross-sectional view of the coatings were observed using a high resolution field emission scanning electron microscope (FESEM). The elemental composition was determined using energy dispersive X-ray spectrometer (EDS) incorporated with FESEM (FEI-Quanta 450FEG). The surface roughness ($R_a$) of the coatings was measured by using a Mitutoyo Surf Test (SJ-201) profilometer. The adhesion strength of the coating on the substrate was evaluated quantitatively by micro scratch test machine (Micro Materials Ltd., Wrexham, U.K.) under a progressive load, using a 25 μm radius Rockwell diamond indenter.

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3. Results and discussion

The XRD technique was used to identify the crystalline phases present in the coatings. Identification of phases is achieved by comparison of the acquired data to that in databases containing standard XRD reference patterns for various materials. In the present work, the Joint Committee on Powder Diffraction Standards (JCPDS) database has been used and all the XRD peaks shown in Fig. 1 matched with the JCPDS reference no. 74–0565 for hydroxyapatite. This indicates that the synthesized bioceramic from eggshells was phase pure HA.

The XRD patterns of MAO coatings on Ti substrate prepared under different concentrations of EHA are shown in Fig. 2. The phases that were detected in the MAO coatings includes HA as the major phase with Ti and TiO$_2$ (anatase and rutile) as the minor phases. The TiO$_2$ layer is believed to be sandwiched between the Ti and EHA after the MAO treatment. However, the intensity of Ti and TiO$_2$ decreased as the EHA concentration increased. According to the XRD results, the E2 sample exhibited the highest HA intensities and hence crystallinity in the

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Fig. 1. XRD signature of as-synthesized EHA powder. All peaks correspond to that of standard HA phase.

Fig. 2. XRD patterns of coatings produced on Ti6Al4V using different concentrations of EHA.
coating structure when compared to E1 and E1.5 samples. During MAO treatment, anatase was initially formed but as the treatment time increases, the temperature in the micro pores or micro discharge channels on the substrate surface would increase thus leading to transformation of the anatase to rutile phase [44]. At high temperatures, rutile is thermodynamically stable while anatase is metastable [45]. The phase transformation rate of anatase to rutile decreases in the coating in the order of E0 > E1 > E2 > E1.5, which may be due to several combinatory factors such as variations in the processing parameters such as electrolyte conductivity, chemistry of the electrolyte, inter-parameter interactions and thermal history of the growing film. Anatase and rutile phases have tetragonal crystal structure and they adhere chemically to hydroxyapatite.

The formation mechanism of EHA/TiO2 composite coating can be described as follows; during MAO treatment, the high voltage generates an electric field between the cathode and anode accompanied by formation of micro discharge channels on the substrate. The temperature in these micro channels could vary between 800 and 3000 K [46] resulting in the formation of ions. Thus, at high localized pressure and high temperature, the titanium ionizes according to the following reaction:

\[
\text{Ti}^4+ \leftrightarrow \text{Ti}^3+ + 4e^{-} \quad (1)
\]

As the time of the reaction extends and titanium dissolves and oxygen will be produced according to Eq. (2).

\[
4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \quad (2)
\]

The oxygen will be release as gas or it will dissolve into the solution as atoms and ionize into O2−. As electrostatic interactions exist during MAO process, OH− and O2− that are negatively charged migrates to the positively charged Ti substrate. The positively charged Ti4+ ions react with anionic compounds such as hydroxyl (OH−) and O2− ions. Thus, leading to the development of TiO2 according to the following reactions:

\[
\text{Ti}^4+ + 2\text{OH}^- + 2\text{H}_2\text{O} \leftrightarrow \text{TiO}_2 + 2\text{H}_2\text{O}^+ \quad (3)
\]

\[
\text{Ti}^4+ + 2\text{O}_2^- \rightarrow \text{TiO}_2 \quad (4)
\]

At the later stage of the MAO treatment, the sodium phosphate in the electrolyte ionizes to Na+ and PO4−3. EHA particles are negatively charged by the ionized PO4−3 and would be attracted to the anode (Ti substrate) and precipitate on the oxidized Ti surface. As the voltage increases, discharging of the micro arc intensifies, leading to high temperature and pressure within the vicinity of the micro channels, leading to consolidation of EHA particles onto the Ti surface. Some of the remnant anatase and rutile would be trapped in the EHA coating as confirmed by the relatively lower intensity peaks for rutile and anatase detected by XRD analysis.

The ATR-FTIR spectra of EHA-based MAO coatings produced at various concentrations of EHA is shown in Fig. 3. The major functional groups identified in the coatings which correlates with the literature [20,47–57] are phosphate, hydroxyl, hydrogen phosphate, carbonate and TiO2 as given in Table 1. More specifically, the ATR-FTIR spectrum confirmed the presence of phosphate group (PO4−3) as represented by the non-degenerated symmetric stretching vibration mode (νs; 950–960 cm−1), triply degenerated asymmetric stretching vibration mode (νas; 1046 and 1158 cm−1) and tetra degenerated bending mode (δs; 545 and 602 cm−1). The presence of hydroxyl group was confirmed by the stretching mode observed in the range of 3623–3634 cm−1 and the broad band for stretching mode of O=H bond at 3300–3600 cm−1 in apatite structure. On the other hand, the strong band centered about 1427 cm−1 together with the narrow band around 870–875 cm−1 are characteristics of the C–O stretching mode of carbonate ions (CO32−). This observation indicates the non-stoichiometric nature of the apatite structure of the EHA coatings. The spectrum also shows the generated stretching mode of hydrogen phosphate (HPO42−,

\[
v_{1}\text{ at 710-730 cm}^{-1}\text{ in apatite structure. Moreover, the results of FTIR spectrum revealed that the Ti–O bending vibration visible around 667 cm}^{-1}\text{ and in the range of 1312–1318 cm}^{-1}\text{ signifies the formation of TiO2 in the coating. The minor bands observed at 2856-2920 cm}^{-1}\text{ correspond to C–H symmetric stretching associated with the eggshell-derived apatite. The P–H stretching modes of band associated with the apatite structure are found between 1980 and 2283-2378 cm}^{-1}\text{. The band in the range of 2132–2164 cm}^{-1}\text{ is attributed to CO which occurred due to the absorption of carbon in the TiO2 structure.}

In addition, the ATR-FTIR spectrum indicates that the band corresponding to PO4−3 at 1046 cm−1 has become significantly sharper with increasing EHA concentration and this can be associated with the improved crystallinity of the HA phase in the coating [58].

The FESEM morphologies of MAO coatings formed on Ti6Al4V substrate at different concentrations of EHA are shown in Fig. 4. All coatings reveal a typical characteristic features of a porous structure formed on the outer layer of the titanium surface. Based on visual inspection, a relatively smooth coating surface was produced for E0 sample when compared to the other coatings containing the EHA addition. During the MAO treatment, micro discharge channels or micro pores were formed when the gas bubbles and molten oxide ejected outward from the discharge channels of micro-arc to the coating. This would result in the formation of a porous network and crater-like structure in the coating layer [59]. It has been reported that considerable microcracks and shrinkage cavity were produced in the micro discharge channels during MAO treatment. The microcracks produced on the surface of MAO coating are due to the influence of thermal stresses in the plasma discharge channels during the rapid solidification of the molten oxides in the electrolyte [60]. Nevertheless, a porous network formation on the outer layer of a crack-free coating surface would be beneficial in enhancing the osseointegration between titanium implant and bone, promoting cell attachment and bone growth [61].

Close examination of the surface topography revealed that the pores of the MAO surface were uneven and irregular in shape. These features are more apparent as the EHA concentration increased. Furthermore, the morphology and composition of the HA coating could be influenced by the electrolyte anionic components which get involved at the anodic surface during the electrochemical reactions [62,63]. It can be observed
The concentration gradient, the Ca\(^{2+}\) ions will be rejected by the anode and this will cause a high oxidation layer under strong micro arc discharge. In the meantime, due to the variation in the surface morphology of the coatings was expected with the addition of different concentrations of EHA to the base electrolyte.

The EDX spectra of the coatings produced at different concentrations of EHA is shown in Fig. 4 (a-d). The characteristic peaks corresponding to Ti, O, Al, Na, P are observed for all coatings. The high content of Ti and O elements is evident due to the oxidation of Ti substrate during MAO treatment. For the coatings formed in the EHA-containing electrolyte, the EDX spectrum revealed the presence of Ca and P elements on the coated surfaces which indicates that the HA has been incorporated into the film during the treatment. The amount of Ca and P increases with increasing EHA concentration which imply that the rate of incorporation of Ca and P into the films is impeded by the addition of anions to the base electrolyte solution under the same experimental conditions.

The Ca and P concentrations in the films formed at different EHA concentrations are presented in Table 2. The highest Ca/P ratio of 1.52 obtained for E2 sample was due to the higher concentration of EHA present in the electrolyte. The decrease in the Ca/P atomic ratio indicates that the Ca\(^{2+}\) ions concentration deteriorates more rapidly than that of PO\(_4^{3-}\) or HPO\(_4^{2-}\). Liu et al. [65] have provided a reasonable explanation for the reduction of Ca/P atomic ratio in the coatings. During the initial stage of MAO process and under strong electric field, the Ca\(^{2+}\) ions will be rejected by the anode and this will cause a high concentration of Ca\(^{2+}\) ions to migrate from the surface of the anode. The Ca\(^{2+}\) ions near the surface of Ti will be incorporated into the oxidize layer under strong micro arc discharge. In the meantime, due to the concentration gradient, the Ca\(^{2+}\) ions in the solution will disperse into the anode surface. As the oxidation time increases and the coating thickness increases, the MAO reaction deteriorates progressively and the amount of Ca\(^{2+}\) ions incorporated into the layer will be decreased. Moreover, the Ca\(^{2+}\), PO\(_4^{3-}\) and HPO\(_4^{2-}\) ions diffusion speed will be decreased within the solution [65]. In addition to the aforementioned elements, it is worth mentioning that Mg peak was observed in E1.5 and E2 coatings. The presences of Mg in the coating layer could be attributed to the eggshells used as the calcium source in the production of EHA. The presences of Mg in the coatings is beneficial since it is known to play a vital role in inducing the proliferation of bone metabolism which influences the osteoclast and osteoblast activity as well as promoting bone growth [66,67].

The cross-sectional views of the EHA coatings are presented in Fig. 5 and their corresponding thickness as measured from the FESEM micrograph is given in Table 3. A denser and thicker layer were observed with increasing EHA concentration. In general, the coatings formed can be classified into two regions i.e. the inner compact layer and the outer layer. During the MAO process, the coating is developed through a process involving external growth towards the coating/electrolyte interface and internal growth towards the substrate. The inwards growth is due to the oxygen diffusion towards the titanium substrate, whereas the exterior progression is attributed to the continuous reaction between the electrolyte with the consolidated coating surface [68-70].

The surface roughness (R\(_a\)) of the uncoated Ti and coated samples are given in Table 3. It was found that the R\(_a\) of the coated samples increased distinctly with increasing EHA concentration (> 0.7 μm) after the MAO treatment when compared to that of the uncoated polished Ti surface (0.18 μm). This high surface roughness of the coatings would be beneficial for orthopedic application since it promotes osseointegration and mechanical locking between hard tissues and the implant [71].

The durability of a coating material plays an important role in determining the functional applications of a coated implant. On this aspect, the service lifetime and quality of the coatings are governed by the adhesive strength between the coated films and substrate material. The scratch test is often used to determine the adhesive strength of coatings. In this test, the critical loads that a coating could sustain would depend on mechanical integrity (cohesion and adhesion) of the coating-substrate and other test parameters such as loading rate, scratch speed, indenter material and indenter tip radius, test environment or it can be related to the film-substrate system such as coating and substrate properties and surface conditions [71,72]. In this work, the scratch test was conducted and the scratch tracks were examine using an optical microscope and FESEM.

Fig. 6(a-d) presents the surface topography of the scratch produced and the graph of load versus scratch length for the coated samples. In the scratch load analysis, the critical loads on the scratch track are determined by the chronologies of the sudden changes along the scratch profile. The critical loads including L\(_c\), L\(_e\) acts as the elastic load, and other test parameters such as loading rate, scratch speed, indenter material and indenter tip radius, test environment or it can be related to the film-substrate system such as coating and substrate properties and surface conditions [71,72]. In this work, the scratch test was conducted and the scratch tracks were examine using an optical microscope and FESEM.
Fig. 4. FESEM images of coatings produced on Ti6Al4V in various EHA concentrations: (a) E0, (b) E1, (c) E1.5 and (d) E2.
and scratch width becomes visible as shown in Fig. 6.

For the EHA-free coated sample (E0), the optical microscope analysis revealed that initially a fine crack was formed inside the TiO₂ coating at a scratch length of nearly 230 μm (Fig. 6(a)) which indicates a cohesive failure within the coating. Such cracks are formed due to the penetration of indenter through the thin film and the inadequate initial load which results in groove formation during the initiation of scratch. An abrupt change in the penetration and load curves takes place when the indenter tip goes deeper into the layer. The coating completely failed (i.e. detached from the substrate) at a scratch length of 472 μm corresponding to a load (L₁) of 1201 mN. Such low adhesive strength of the E0 sample can be attributed to the low coating thickness and the rather weak bonding of the anatase and/or rutile TiO₂ layer and the Ti surface. This result is in good agreement with that reported by de Souza et al. [73] who used a sharp Berkovich indenter for the scratch test and observed a cohesive failure of thin TiO₂ based PEO coating on titanium at loads below 1000 mN.

For the EHA-coated samples, the optical analysis showed a partial and intermittent delamination along the scratch track (Fig. 6(b–d)). It can be observed that the adhesion strength of the E1, E1.5 and E2 coatings were higher than that of the E0 coating. For the E1 sample, the coating failed at scratch length of about 630 μm corresponding to a critical load of 1712 mN. The localized tensile stresses that were generated behind the indenter during the initial stage of scratching process resulted in crack initiation followed by subsequent propagation. Moreover, when the load is applied progressively, and when the critical thickness is reached the coating tends to be too stiff to buckle. As a consequence, compressive shear stress forms through the thickness of the coating. The generated compressive shear stress ahead of the moving indenter leads to formation of small periodic localized hemispherical coating chipping along the side of the scratch track. In addition, when the indenter moves forward, the stress is increased, leading to propagation of further chips along the trackside of the scratch as illustrated in Fig. 6(b) which is shown by the fluctuation in the load curve during the scratch test. For E1.5 coating (Fig. 6(c)), the first small area of delamination took place at the scratch side when it reached a scratch length of 402 μm (L₁) and the intermittent delamination extended until it failed under a critical load of 2251 mN (L₂) corresponding to a scratch length of 809 μm. In contrast, E2 coating (Fig. 6(d)), the same failure mode where the first coating delamination was detected at a scratch length of about 389 μm (L₁), and the delamination continued intermittently until the substrate was completely exposed at a critical load of 1949 mN (L₂) corresponding to a scratch length of 712 μm. For E1.5 and E2 coatings, no cohesive cracks were observed at lower loads, indicating a plastic deformation behaviour of the coating. The E1.5 sample exhibited the highest coating adhesive strength due to the stronger bonding between the TiO₂ layer and the Ti surface, and the uniform distribution of EHA particles in the coating. Although, the E2 coating was thicker, it exhibited lower adhesive strength compared to E1.5 (i.e. based on the critical load of 2251 mN @ E1.5 > 1949 mN @ E2). In general, thicker coatings would have more defects across the thickness and higher porosity which could act as sites for crack initiation at moderate loads thus resulting in lower adhesion strength. Another plausible explanation for the relatively low adhesion of E2 coating may be associated with its non-homogeneous layer due to the agglomeration of the EHA

### Table 2

Elemental composition of EHA coatings on Ti6Al4V surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>E0</th>
<th>E1</th>
<th>E1.5</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca, at%</td>
<td>7.25</td>
<td>8.86</td>
<td>13.66</td>
<td>16.15</td>
</tr>
<tr>
<td>P, at%</td>
<td>1.25</td>
<td>1.38</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>Ca/P ratio</td>
<td>7.25</td>
<td>10.86</td>
<td>18.81</td>
<td>24.49</td>
</tr>
</tbody>
</table>

### Table 3

Variations of thickness and roughness of coatings produced with different EHA concentrations.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Coating thickness (μm)</th>
<th>Roughness (Ra) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>–</td>
<td>0.18</td>
</tr>
<tr>
<td>E0</td>
<td>8.53</td>
<td>0.76</td>
</tr>
<tr>
<td>E1</td>
<td>10.65</td>
<td>1.63</td>
</tr>
<tr>
<td>E1.5</td>
<td>12.72</td>
<td>1.81</td>
</tr>
<tr>
<td>E2</td>
<td>15.57</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Fig. 5. FESEM cross sectional view of coated substrates formed at different concentrations of EHA: (a) E0, (b) E1, (c) E1.5 and (d) E2 samples. Keys: (1) epoxy resin region, (2) MAO coating region, (3) substrate region.
particles in the electrolyte during the MAO process. In general, increasing the EHA content in the electrolyte could cause an increased in the electrostatic force of attraction between the particles in the suspension, thus leading to agglomeration. This in turn would result in a non-uniform deposition of the EHA particles along the surface of the substrate. This is consistent with the literature \[74\] where it has been shown that the increased of HA concentration in the base electrolyte resulted in an intermittent delamination at the scratch track.

The coated substrates (E1.5 and E2) were investigated further in order to examine the diffusion and the chemical composition of the coating layer along the scratch track. The elemental distribution analysis for both samples are shown in Fig. 7. It can be observed that higher critical loads led to more deformation at the scratch track and edge, which results in chipping and some spallation on the sides of the scratch area. However, no interfacial fracture between the coating and substrate was detected, which indicates that the mechanical interlocking and chemical bonding between the coating and substrate was adequate. Besides that, from the line scan analysis along the scratch track, it can be seen that the elemental constituents differ along the scratch track until it reached the failure point where Ti peaks increased dramatically. The fading titanium signal at the beginning of the scratch can be due to the interposed layer, which decelerates and absorbs the characteristic X-rays of titanium.

The electrochemical experiment conducted on the samples revealed that the uncoated Ti substrate recorded a corrosion current density ($i_{\text{corr}} = 1.211 \mu A$) which is lower than that measured for the MAO...
would act as the anode and the oxide coating layers and react with the Ti substrate. The inside of the pore coatings can provide easy path for the corrosive media to penetrate into the substrate, thus enhancing the corrosion resistance of the titanium substrate. This mechanism is explained as follows; the corrosion resistance of the coatings is mainly influenced by porosity and thickness of the coating. The pores in the coating can provide easy path for the corrosive media to penetrate into the coating layers and react with the Ti substrate. The inside of the pore would act as the anode and the oxide film on the substrate as the cathode which complete the cell and cause an increase in the current density. When the inner Ti substrate is exposed to the PB solution, it will cause an electrochemical reactions at the interface of the substrate, thus enhancing the corrosion resistance of the Ti substrate.

4. Conclusions

In this research, phase pure hydroxyapatite was synthesized through reacting waste calcined eggshells with phosphoric acid. Eggshell-derived hydroxyapatite coatings of uniform thickness have been deposited successfully on the surface of Ti6Al4V alloy at different concentrations of EHA in an electrolyte consisting of Na2HPO4, 12H2O solution by using micro-arc oxidation method. XRD and ATR-FTIR analysis confirmed the presence of hydroxyapatite as the major phase along with anatase and rutile TiO2 as the minor phase in the coated substrate. The crystallinity of the HA phase and the thickness of the coating were found to increase with increasing EHA concentration during the MAO treatment. The optimium amount of EHA to produce a well-defined coating by MAO method was found to be 1.5 g/L (E1.5). At this concentration, the coating exhibited the highest adhesive strength followed by the E2 sample, attributed to the good bonding between the EHA and oxide layer as well as the uniform distribution of EHA particles in the coating. The roughness of the coating was also found to increase along with the Ca/P ratio with increasing EHA content. A Ca/P ratio of 1.54 was attained for the E2 sample and this is in good agreement with that of human bone. The electrochemical experiment showed that both, the E1.5 and E2 coatings exhibited the lowest current density and therefore were effective in enhancing the corrosion resistance of the Ti substrate.

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References


Fig. 7. FESEM images of the scratch tracks within EHA coated samples for (a) E1.5 and (b) E2 samples accompanied with their corresponding line scan analysis.


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