Coating of Nanotube Ti-6Al-4V Alloy with Hydroxyapatite-Chitosan Composite by Electrophoretic Deposition Method

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Abstract

Bone implant material composed of Ti-6Al-4V alloy is typically used due to its biocompatibility and corrosion resistance. However, this alloy is not bioactive which makes it easy to release cation Al and V when implanted into the human body. Therefore, this study aims to form a nanotube structure on the surface of Ti-6Al-4V alloy and coat hydroxyapatite (HA)-chitosan composite onto the nanotube Ti-6Al-4V alloy. Nanotube synthesis was carried out by the anodization method on NH_4F 5% solution at 20 V, for 1 hour.

The result of scanning electron microscope characterization demonstrates that the nanotube was formed heterogeneously and was not uniform with a hole diameter with a size of 2–3 μm. The HA-chitosan composite coating of the nanotube was performed by the electrophoretic deposition method at 100 V for 1 hour. Coating was spread evenly on the entire alloy surface. There was no significant difference between HA-chitosan composite coating on the nanotube area and the non-nanotube area. X-ray diffraction and Fourier transform infrared analysis showed that HAp-chitosan composite successfully coated the nanotube Ti-6Al-4V alloy.

Keywords: Anodization, chitosan, hydroxyapatite, nanotube, Ti-6Al-4V.

Introduction

Titanium (Ti) and alloys have biomechanical properties (mechanical properties corresponding to body tissues) that are better compared to other metals, are inert and have high corrosion resistance i.e. are spontaneously able to form layers of TiO_2 on a surface that is often used for implant materials[1].

The metal of Ti-6Al-4V alloy has high biocompatibility, corrosion resistance, low density and low elastic modulus[2]. However, it has poor bioactive properties[3]. The bioactive properties of Ti-6Al-4V can be enhanced by modifying the metal surface into a grown oxide layer[4]. The modification of metal surfaces into nanotubes has several advantages namely, improved strength of adhesion and attachment between the substrate and the metal surface[5], high specific surface area, ion exchange ability and the ability to easily become filled by organic or inorganic materials for composite manufacture[6]. The methods for making nanotubes include anodizing, hydrothermal and sol-gel[7].

The advantage of the anodization method is that nanotubes are obtained in the form of nanotube arrays[8]. However, the release of metal ions such as Al and V cations of Ti-6Al-4V alloys causes inflammation, local toxicity, tissue damage and joint relaxation[9]. Karokaro et al[10] mentioned that the release of metal ions can be overcome by coating biomaterials that are biocompatible, bioactive and able to resist corrosion of metals such as hydroxyapatite (HA). HA has structural similarities with bone and has the ability to repair and accelerate the formation of new bone, does not damage the immune tissue, is biocompatible, is bioactive and does not cause inflammation[11]. HA was synthesized from snail shells (*Bellamya javanica*) and contains high levels of calcium. The calcium content of the snail shell is 88.54%[12]. The mechanical strength of HA can be increased by composting HA with chitosan[13].

Chitosan is a nontoxic biopolymer that is biodegradable, biocompatible[14] and has antibacterial activity[15]. The coating of HA chitosan composite on metal surfaces was performed by using electrophoretic deposition (EPD) method. The advantages of the EPD method are that it uses low temperature, involves deposition of the solution directly[15], requires preparation of simple tools and has easily controlled phase composition[16]. The aims of this research are to form nanotube structures on the surface of Ti6Al-4V alloys and coat Ti-6Al-4V nanotubes with HA-chitosan composites.

Material and Methods

Synthesis of HA: HA was synthesized from two types of precursors namely Ca and P. Ca precursors which were obtained from $Ca(OH)_2$ results of the preparation of snail shells of rice fields. Meanwhile, $(NH_4)_2HPO_4$ was used as a precursor P. Both types of precursors were prepared with a solution of 0.5 M $Ca(OH)_2$ and 0.3 M $(NH_4)_2HPO_4$. The solution of 0.3 M $(NH_4)_2HPO_4$ was added dropwise into 0.5 M $Ca(OH)_2$ suspension solution using a burette while stirring with a magnetic stirrer. During the mixing process, the temperature conditions were preserved at 40±2°C and pH 10 for the reaction mixture. In this synthesis, the pH of the reaction mixture was checked periodically using a universal pH indicator and corrected with the addition of NH_4OH if the pH was less than 10.

The reaction mixture was decanted for 24 hours at room temperature. Subsequently, the reaction mixture was synthesized for 2 hours and then centrifuged at 4500 rpm for 15 minutes. The supernatant and pellet were filtered using a Büchner mouthpiece, while being rinsed with distilled water. The pellet or precipitate was dried in an oven at 105°C for 3 hours. After drying, the precipitate was pounded until smooth using a mortar. The powder was sintered at 900°C for 2 hours and then cooled in a desiccator.

Formation of Nanotubes on Surface Ti-6Al-4V Alloy[15]: A metal Ti-6Al-4V alloy with a 12 mm and 5 mm thick diameter was used. Pieces of the metal alloy were rubbed using SiC paper or 320-1500 grit sand paper. Subsequently, the metal was cleaned with ethanol, acetone and distilled water ultrasonically (sonication) for 15 minutes. Pieces of Ti-6Al-4V were immersed in a solution containing 3 mL of concentrated HNO_3, 1 mL NH_4F 5% (w/v) and distilled for 20 seconds. The metal was then removed, rinsed with distilled water and dried at room temperature.

The formation of nanotubes on the surface of Ti-6Al-4V alloy was performed by the anodizing method. Pieces of Ti-6Al4V were anodized in 5% NH_4F (w/v) solution with 20 V from Direct Current (DC) and Alternating Current (AC) for 1 hour. The anodizing process was carried out with two electrodes i.e. Pt electrode as the cathode (negative pole) and piece Ti-6Al-4V as the anode (positive pole). The distance between the cathode and the anode was set to 4 cm. After the anodizing process, pieces of Ti-6Al-4V were rinsed with aquades and dried at room temperature.

Nanotube Ti-6Al-4V alloy coating with HA Chitosan Composites: The 2% chitosan solution was taken as much as 1.5 mL and then dissolved into 25 mL of ethanol. Subsequently, 0.2 g HA was added bit by bit while stirring using a magnetic stirrer. The formed HA-chitosan solution was connected to two electrodes i.e. Pt electrodes as positively charged electrodes and Ti6Al-4V alloy that are modified into nanotubes as negatively charged electrodes targeted for coating. The coating process by the EPD method was carried out with a voltage of 100 V for 1 hour. After the coating process was complete, the alloy was dried so that the HA-chitosan composite attaches strongly to the nanotube Ti-6Al-4V alloy.

Results and Discussion

The anodization of Ti-6Al-4V alloy was carried out with two variations of current, namely, AC and DC current. This variation aims to prove and determine the currents that can form the structure of the nanotubes. Anodized results performed for 1 hour with AC and DC current indicate that the nanotube was only formed with DC current. The success of the formation of nanotubes can be observed by an optical microscope which is seen as a black oxide layer on the metal surface (fig. 1b). According to Kaczmarek-Pawelska and Krasicka-Cydzik[17], the oxide layer comprises TiO_2, VO_2, V_2O_3 and V_2O_5.

The reaction is as follows:

$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$
$6Al + 9H_2O \rightarrow 3Al_2O_3 + 18H^+ + 18e^-$
$4V + 10H_2O \rightarrow 2\ V_2O_5 + 20H^+ + 20e^-$

Anodization with a DC current involves a direct current. With DC currents, the electric current carried by the F^- ion in the electrolyte solution moves in the same direction and then implies directly the formation of a small hole that acts as the core in pore formation before the nanotubes are formed. Meanwhile, the anodizing process with AC current involves an alternating current, so that the mobility of F^- ions in the electrolyte solution moves back and forth and does not have direct implications for chemical dissolution for nanotube formation. In addition, anodizing with AC currents causes the formation of a transverse and centered oxide layer on one part (fig. 1b), so that nanotubes cannot be formed.

The result of the preparation with SEM (fig. 2) shows that nanotubes with a hole diameter of about 2-3 μm are formed from anodizing with DC currents in Ti-6Al-4V metal alloys. However, the nanotubes were heterogeneous and not uniform. The heterogeneity of the nanotubes is due to the α and β phases that make up the Ti-6Al-4V alloy. According to Kaczmarek-Pawelska and Krasicka-Cydzik[17], nanotubes are more easily formed in the α phase than in the β phase. This is due to the presence of vanadium structures that dominate the β phase and are soluble in an electrolyte solution containing F-ions. According to Macak et al[18], the α and β phases of Ti-6Al-4V metal alloys can be observed in micrograph results. The dark area is the α phase while the lighter region represents the β phase (fig. 2b).

In this study, the Ti-6Al-4V metal alloy nanotube coating process was carried out by EPD method at 100 V for one hour. Ti-6Al-4V coated with HAp composite is characterized by FTIR and SEM. The establishment of FTIR was conducted in order to identify the functional group of the composite. Based on the FTIR spectrum, the presence of chitosan is shown by the N-H absorption bands at a wave number of 3427.51 cm^{-1}, C-H absorption bands at 2922.16 cm^{-1} and C-N absorption bands at 1562.34 cm^{-1}. Additionally, there is a vibration of OH-fracture of chitosan and HA at 3568.31 cm^{-1}.

The other HA characteristic absorption bands appear at 1047.35 cm^{-1} indicating vibration stretching asymmetry of PO_4^{3-}. Bending vibrations of PO_4^{3-} also appear at wave numbers 632.65 cm^{-1}, 601.79 cm^{-1} and 569.00 cm^{-1}. Based on these data (fig. 3), it is evident that the compound attached to Ti-6Al-4V alloy is a HA-chitosan composite. However, the emergence of CO vibration from CO_3^{2-} on wave numbers 1456.26 cm^{-1} and 1419.61 cm^{-1} indicates that the HA of the purity synthesis is poor. According to Ramli et al[19], CO_3^{2-} can replace the OH^- position in HA to form $Ca_{10}(PO_4)_6CO_3$ (type A apatite carbonate) or replace PO_4^{3-} form $Ca_{10}(PO_4)_3(CO_3)_3(OH)_2$ (apatite carbonate type B).

The X-ray diffraction pattern of HA appears at 31.86°, 32.1°, 32.82° and 33.94° (Fig.-4). X-ray diffraction patterns of Ti also appear on the diffractogram based on identification with JCPDS No. data 00-044-1294. X-ray diffraction pattern on Ti appears at angles of 40.28° and 78.12°. X-ray diffraction patterns of Al and V do not appear, since the two elements are composite Ti-6Al-4V alloys of less than 10% composition. Similarly, chitosan does not show the pattern of X-ray diffraction on the diffractogram. Marist[20] revealed that the chitosan X-ray diffraction pattern of HA-chitosan composites appears if the chitosan content in the composite is more than 30%.

The coated sample results are characterized by SEM to determine the morphology of HA-chitosan composites. Based on the results of the assay by SEM, the morphology of the HA-chitosan composite has an agglomerated granular shape and is smaller in size compared to HA (fig. 5). The shrinkage of granular size from 40 μm to pure HA to about 5 μm for HA-chitosan composites is because HA is incorporated in the chitosan matrix. The chitosan matrix causes the HA to become denser. Therefore, HA made composites with chitosan can increase mechanical strength.

Fig. 1: Metal alloys Ti-6Al-4V (a) before anodization (b) anodized product with DC current and (c) anodized product with AC current

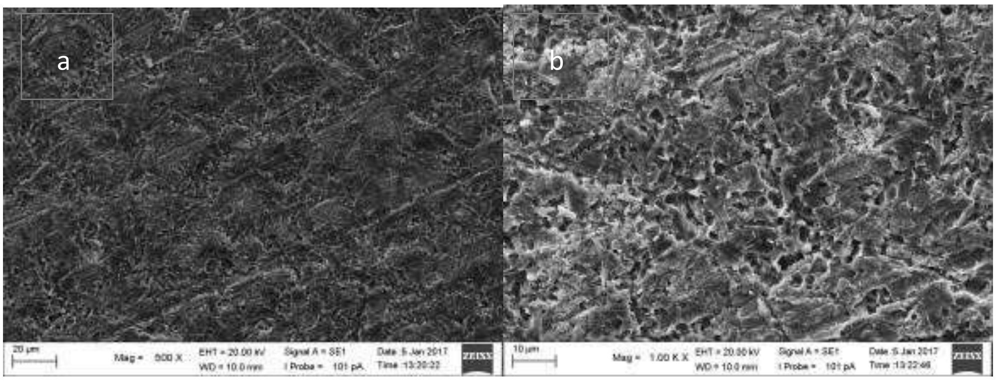

Fig. 2: The morphology of Ti-6Al-4V metal alloy alloys at (a) 500x magnification and (b) 1000x magnification

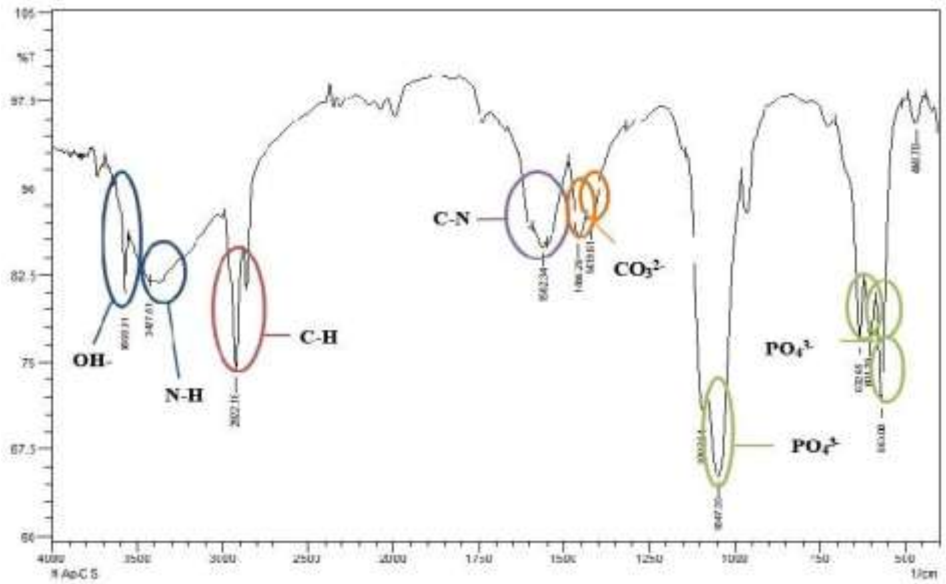

Fig. 3: The FTIR spectrum HA-chitosan

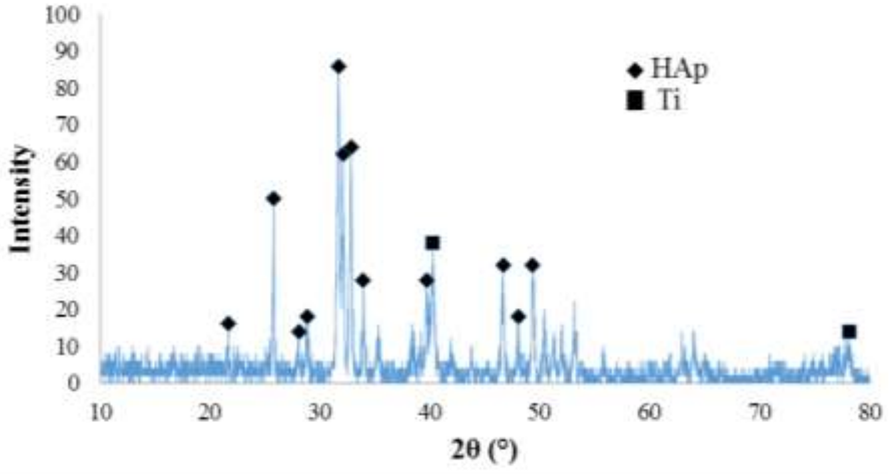

Fig. 4: X-ray diffraction patterns of the HA-chitosan coated sample.

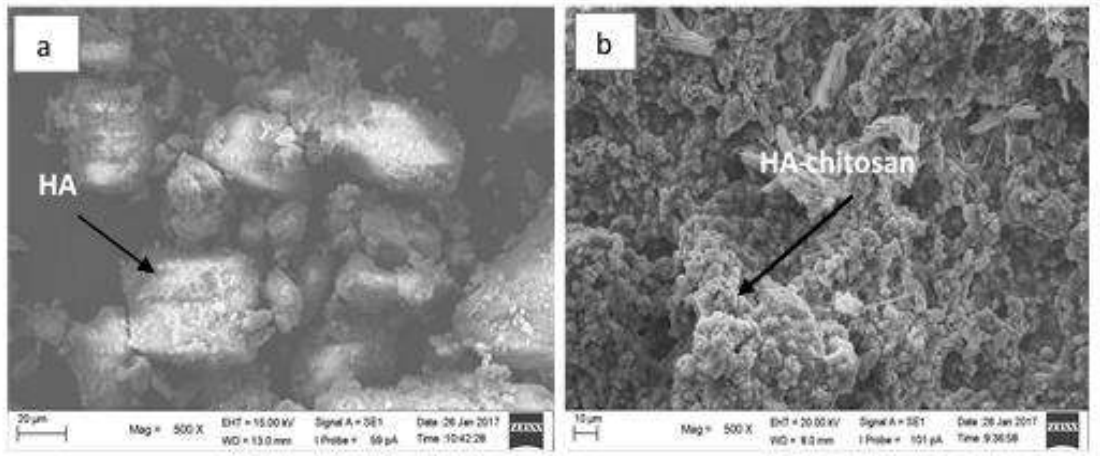

Fig. 5: Morphology of SEM: a) HA, b) HA-chitosan coated

Conclusion

The development of nanotube formation of Ti-6Al4V alloy was not successfully performed optimally, since the result of the SEM stirring shows the diameter of the nanotube hole to be about 2-3 µm and was formed heterogeneously. The result of coating with HA-chitosan composite was evenly distributed on all metal surfaces. The composite coated on Ti-6Al-4V alloy nanotubes has an agglomerated granular form morphology of a smaller size compared to pure HA. The establishment of XRD and functional group identification by FTIR indicates that the HA-chitosan composite has coated Ti-6Al-4V metal alloy nanotubes.

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