PREPARATION AND CHARACTERIZATION OF CHITOSAN/HYDROXYAPATITE SOL-GEL COATING ON Ti-6Al-4V

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A biocomposite coating containing chitosan and hydroxyapatite was developed on Ti-6Al-4V substrate by a sol-gel method in order to obtain a biocompatible and antimicrobial implant surface which can be used to create a smooth transmucosal region for a faster and better wound healing and an increased bioactivity. The coatings characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and differential thermal analysis (DTG). Scratch test was carried out to evaluate the adhesion between the coated film and the substrates. The critical load at which the coating film was peeled off from the substrate is determined by using the spherical diamond stylus. The results revealed that the coating roughness is approximately 0.23. The critical load for debonding the coating film from the substrate was determined between 6 to 11N. Only a little wear debris was come out from the coating film in the initial stage of a small-applied load. With increasing the load, the coating film became crushed and finally worn away.

Keywords: Chitosan, hydroxyapatite, sol-gel.

INTRODUCTION

Biomaterials can be classified as synthetic and natural biomaterials. Synthetic biomaterials have some disadvantages because of their structure, composition that is not similar to original tissues/organs and due to their biocompatibility. Naturally obtained biomaterials like chitosan are generally applied to replace or restore structure and function of damaged tissues/organs. They have properties in order to improve cell adhesion, migration, proliferation, and differentiation. Especially, when natural biomaterials implanted into a defective area, they can increase the attachment and migration of cells from the surrounding environment (Bao *et al*., 2013).

Chitosan property of osteoconductive is suitable for engineering applications in hard tissues, but its mechanical properties and biological activities need to be enhanced (Yun *et al*., 2013). In order to increase the mechanical properties, chitosan can be modified by blending with other natural polymers like silk, alginate, gelatin or ceramics, such as, tricalcium phosphate and hydroxyapatite (Thein-Han and Misra, 2009; Silva *et al*., 2007). The development on the production of hybrid HA/Chitosan coatings is an area of increasing interest. Hybrid HA coatings with chitosan can enhance the adhesive strength of the HA coatings. Chitosan was selected in the fabrication of hybrid HA coatings is due to its magnificent film forming properties and the cationic nature in aqueous solutions. It has an antimicrobial activity, good chemical stability, good biocompatibility, good advanced mechanical and other properties that has been utilized in biomedical implants (Isa *et al*., 2012).

Titanium and its alloys are the most common metallic biomaterials that used for medical implants due to their low elastic modulus, high strength, excellent biocompatibility and excellent resistance against corrosion (Adell *et al*., 1981). However, because of the differences in chemical composition and structure, there is lots of inflammatory effect around metallic implants observed (Lee *et al*., 2009). One of the solutions is coating the titanium substrates with Hydroxyapatite (HA). Hydroxyapatite is commonly used in bioceramic due to similarities with human skeletal system, which increase the osteoconductive bonding of implants with surrounding tissues (Milella *et al*., 2001).

HA coatings, produced by plasma spraying (Zhang *et al*., 2006), have been shown clinical problems such as delamination, which leads to the premature loosing of implants (Bloebaum *et al*., 1994). The sol-gel process ensures that an attractive method to others due to the easy occurring of crystalline films at relatively lower processing temperatures, higher purity and homogeneity, thin films, simple and easy method of preparation (Im *et al*., 2007). It is convenient for complex shapes like coatings and the main advantage of this process is that the properties of the surface not change at all (Brinker and Scherer, 1990).

The purpose of this research was to reveal the effect of HA/Chitosan on the properties of the deposited coating on Ti-6Al-4V alloys. The composition, phase structure, microstructure and morphology as well as the mechanical features of the HA/Chitosan sol-gel coating are presented and discussed.

EXPERIMENTAL PROCEDURE

Materials and Sample Pre-treatment

The Ti-6Al-4V alloys in this study was cut into 10 mm x 10 mm x 2 mm discs. These discs were then chemically stigmatized with sand blasting with Al_2O_3 (250 µm) particles (MKK-975 sand blaster) and ultra-sonically cleaned, for 15 min, in distilled water, absolute ethanol and acetone, respectively, in order to remove the macro-level surface defects and contaminants. Finally, all samples were dried at 60°C in an incubator for 1h.

Preparation of the HA/Chitosan Sol and Coating

HA powders were synthesized by a sol-gel method. Precursors of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and phosphoric pentoxide (P_2O_5) were added into absolute ethyl alcohol in order to prepare the solutions with a certain molar ratio. These two powders were dissolved separately in absolute ethyl alcohol with different amounts to obtain a theoretical Ca/P ratio of 1.67. Phosphoric pentoxide solution was added at the calcium nitrate tetra hydrate mixture in a drop wise manner after stirring for 6 hours. The final mixture was aged until it turned to opaque. After aging, the mixture was left in water bath for 1h at 60°C. In addition to precursors of $Ca(NO_3)_2 \cdot 4H_2O$ and P_2O_5 samples, Chitosan added to the final mixture with a certain molar ratio. The viscosity of the solution was adjusted by evaporating ethanol solvent at 80°C before dipping. Titanium substrates were immersed in the solution for 1 minute, dried at 80°C in air for 12h. This step repeated several times to meet the requirement of the thickness.

Analysis Techniques

Ti alloys, HA/Chitosan composite coating were examined by means of both SEM and XRD measurements. Scanning electron microscopy (SEM) was performed with a JEOL JSM–6335F, JSM 6600 microscopes. The procedure employed with an electron probe which has a voltage of 20 kV. Before the SEM observations, the samples were coated with Au-Pd. The phase transformation and compound formation were investigated by X-ray diffraction (XRD) measurements were performed by means of a Bruker D8. The XRD measurements were performed on a stage using a radiation of wavelength λ=1.5406 Å X-ray source with a step rate of 0.02° per s. HA powder, which used in coating procedures observed with SEM for determine elements ratio. The EDS analysis confirmed that calcium and phosphorous are present in the coating in a ratio of 1.67.

RESULT AND DISCUSSION

Microstructure and Composition Characterization

The XRD patterns of the synthesized HA/Chitosan powder are represented by the Figure 1 compared with standard HA (ICDD 01-074-9780). XRD analysis of the obtained coating was made on titanium has been proven (ICDD 00-044-1294). The results revealed the presence of HA characteristic peak at 25.99°, 31.75°, 33.65° and 40.68°.

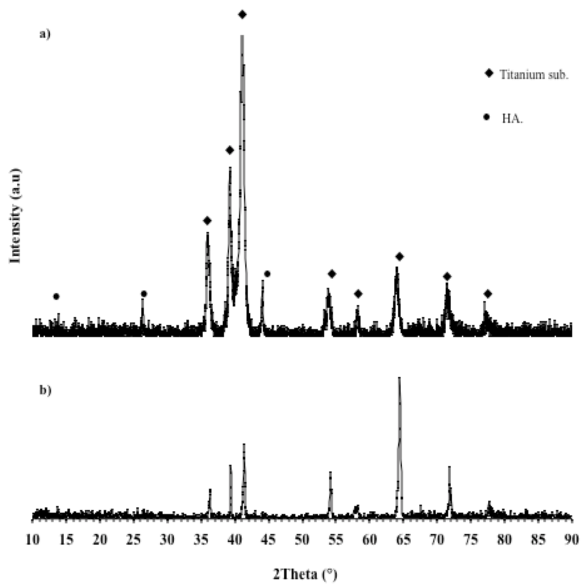

Figure 1. XRD of HAp-chitosan coating a) HA/Chitosan b) Ti Alloy

In Figure 2 the scanning electron micrograph of HA/Chitosan coating at different magnifications is given. When chitosan was added into the HA solution, the morphological structure of the coating was significantly changed from flower-like structure to flake-like structure interconnected with net-like structure of chitosan.

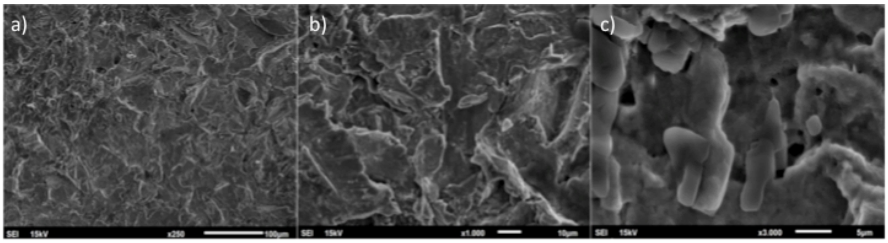

Figure 2. SEM of HA/Chitosan coatings

In Figure 3 as a result of scratch test coating roughness is approximately 0.23. The critical load for debonding the coating film from the substrate was determined between 6 to 11N. Only a little wear debris was come out from the coating film in the initial stage of a small-applied load. With increasing the load, the coating film became crushed and finally worn away.

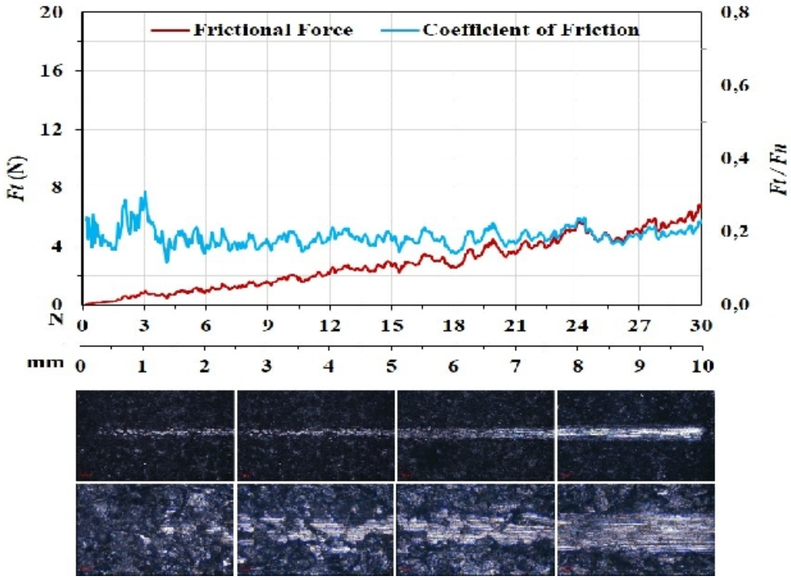

Figure 3. Scratch Test results of the HA/Chitosan coated Ti substrates

CONCLUSION

The preparation of HA/Chitosan coatings on the Ti substrates was achieved by sol-gel method with Ca/P ratio being 1.67. Surface observations, XRD pattern, were investigated, respectively. XRD pattern of HA/Chitosan coating proved that thin film obtained successfully on substrate. The insertion of chitosan has extremely affected the surface morphology and structural characteristics of HA coatings deposited on Ti substrate. The chitosan content in the formed hybrid HA/Chitosan coatings will be increased with increasing chitosan concentration in the deposition solution. In this research, it is obvious that the presence of high amount of chitosan in the deposition solution has prevented the HA formation and makes the chitosan determinant in the coatings formation. In addition to this, doping of hybrid HA coatings with chitosan improved the adhesive strength of the HA coatings.

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