Electrochemical Evaluation Of Hydroxyapatite/Halloysite Nanotube/Polyvinyl Pyrrolidone Composite Coating On TI-6AL-4V Alloy For Orthopedic Applications

D. Bhagya Mathi[1*], D. Gopi[2], L. Kavitha[1]
[1]Department of Physics, School of Basic and Applied Sciences, Central University of Tamil Nadu, Thiruvarur- 610 005, Tamil Nadu, India
2 Department of Chemistry, Periyar University, Salem 636 011, Tamil Nadu, India
*bhagyamathi.phy@students.cutn.ac.in

Abstract:

Excellent mechanical properties, corrosion resistance and favorable biocompatibility of Ti-6Al-4V alloys have made them to receive persistent attention as orthopedic implant. However, its inadequate osseointegration property is a major hindrance for such applications and for this reason, it is important to introduce bioceramic-polymer coatings on the metallic surface to attain true adhesion between the implant and bone. Thus, the present study deals with the development of composite coatings of HAP/HNT/PVP on Ti-6Al- 4V alloy by electrophoretic deposition method. The coatings were characterized Fourier Transform Infrared Spectroscopy (FTIR) which revealed the presence of functional groups. Scanning Electron Microscopy (SEM) demonstrated the morphology. The elemental analysis were done by Electron Dispersive X-Ray Analysis (EDAX). The results of potentiodynamic studies in the simulated body fluid solutions showed that the HAP/HNT/PVP coated Ti-6Al-4V provided better corrosion protection. Hence, HAP/HNT/PVP composite coated Ti-6Al-4V alloy might be a promising material for fabrication of bone implant.

Keywords: Halloysite Nanotubes, Electrochemical impedance spectroscopy, Hydroxyapatite, Simulated Body Fluid, Orthopedic implant.

1. Introduction

There have been extensive development in the accessibility of appropriate metals and metal alloys for orthopedic and dental implants. In the class of metals and metal alloys, Ti-6Al-4V alloys are garnering attraction and are used clinically as orthopedic surgery implants because of their excellent mechanical properties, their corrosion resistance, and their good biocompatibility. Ti-6Al-4V develop a highly stable surface oxide layer when exposed to air or to aqueous media, which is responsible for bone-bonding characteristics of Ti-6Al-4V implants. Ti-6Al-4V implants provide a bioinert surface for adherence and osseoconduction of surrounding bone cells that sparkled progression of titanium alloys for usage in orthopedics[1]. However, when pure metal and metal alloys are implanted into a corrosive physiological in vivo environment, the metal surface may be distorted and exposed to release a large amount of metal ions to the biological fluids and tissues in the body. Ideally, the modification of the implant surface through composite coating was proposed to prevent leach out of metal ions and also to enhance osseointegration between materials and bone tissue[2]. Bone is a multiphase composite, with the main constituents of bone being collagen matrix and assembled hydroxyapatite (HAP) crystals [$Ca_{10}(PO_4)_6(OH)_2$]. HAP with high biocompatibility, osteoconductivity, stability and non-inflammatory properties are widely used as coatings for implants. As HAP coating could not maintain long-term stability due to lack of mechanical strength, it is obligatory to improve the mechanical properties of the HAP coatings without compromising its biocompatibility. Since there is no distinguishedmaterial available to accomplish all the necessary requirements for biomedical applications, development of composites as a substitute for bone

repair has become mandatory[3]. The properties of HAP can be upgraded by the addition of reinforcing material named Halloysite Nanotubes (HNT). Halloysite nanotubes (HNTs), are naturally occurring aluminosilicates with nano-tubular structures. HNTs have drawn much attention to utilize in areas as biomedical implant, corrosion protection coating, and drug delivery system because of the unique properties such as enhanced tensile modulus, strength, non-toxicity and corrosion resistivity, andbiodegradability[4].

The desirable properties of HAP/HNT composite can be further improved by the addition of a suitable biopolymer, Polyvinyl Pyrrolidone (PVP) to make it potential in bone repair and regeneration. PVP has found a wide variety of applications in the biomedical field because of its useful properties including non-toxicity, biocompatibility, high hydrophilicity, good complexation properties, and film-forming ability**.** an alternative substance for autogenous free bone grafting. It is the most prominent bioactive material since it forms a chemical bonding to bone and is widely used andinvestigated[8].

Several methods such as sol–gel, plasma spraying, pulsed laser deposition, electrophoretic method, etc., have been reported so far for the deposition of composite coatings onto implant surfaces. Among these, the electrophoretic deposition (EPD) method has attracted attention for the deposition with controlled rate and to produce homogeneous and dense coatings[3]. This study deals with the successful development of Hydroxyapatite/ Halloysite Nanotubes/ Polyvinyl Pyrrolidone (HAP/ HNT/PVP) composite coatings on Ti-6Al-4V by electrophoretic deposition. The surface characteristics were assessed by Fourier transform infrared spectroscopy. The morphological features were analyzed by high resolution scanning electron microscopy and energy dispersive X-ray analysis. The bioresistivity of the coatings were investigated in simulated body fluid solution by electrochemical techniques such as potentiodynamic polarization which demonstrated that HAP/HNT/PVP coating on Ti-6Al-4V have an impact in improving the anti-corrosion ability. Thus, HAP/HNT/PVP coated Ti-6Al- 4V is efficaciously developed so that it can serve as a prospective orthopedicimplant.

2. Experimental

2.1 Materials

Commercially available calcium nitrate tetrahydrate ($CaNO_3 \cdot 4H_2O$), Halloysite nanotubes (HNT), di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), and polyvinyl pyrrolidone purchased from Aldrich Chemical Co. (Aldrich, India), were used for the development of HAP/HNT/PVP composite coating on Ti-6Al-4V alloy by electro deposition. All chemicals were of analytical grade and were used as received, and deionized water was used throughout theexperiment.

2.2 Synthesis of HAP/HNTcomposite

0.45 M Calcium nitrate dihydrate ($Ca(NO_3)_2.2H_2O$) and 0.25 M $(NH_4)_2HPO_4$ are to be dissolved in deionized water separately and the solutions were to be mixed in the targetratio 1.67. Then , halloysite nanotubes (0.5 g) are dispersed in 100 ml of distilled water under ultrasonication and are added into the electrolyte solution. The solution is vigorously stirred for3h.The pHmustbemaintaine dat 10. The precipitate is wash edrepeatedly with ethanol and water. It was then filtered, washed, dried at 110 °C for 12 h, and ground into a fine powder.

2.3 Synthesis of HAP/HNT/PVPcomposite

To 1.5 g of HAP/HNT composite mixed in equal amount of ethanol-water mixture, 0.5 g of Polyvinyl pyrrolidone (PVP) were added byultrasonication for 1 h. The resultant HAP/HNT/PVP solution was further stirred for 2 h. Then the solution is filtered, washed, dried at 80 °C for 12 h, and ground into a fine powder. Finally HAP/HNT/PVP composite has been obtained.

2.4 Preparation of thespecimen

Ti-6Al-4V alloy, with composition (wt %) 5.7 Al, 3.85 V, 0.18 Fe, 0.038 C, 0.106 O, 0.035 N, and balance titanium, was used in the present study. Pieces of Ti-6Al-4V alloy with a size of 10 × 10 × 3 mm were cut, embedded in epoxy resin leaving area of 1 $cm^2$for exposure to the electrolyte and were designed as the cathode substrate for the electrophoretic deposition of HAP/HNT/PVP composite. Prior to deposition, the samples were abraded with different grades of SiC emery papers

from 400 to 1200 grit, washed with distilled water, ultrasonically degreased with acetone to remove surface impurities, and then finally washed in deionized water and dried at room temperature of 30 °C for furtherpurpose.

2.4 Electrophoretic Deposition of CNTs/CMC/M-HAP Composite on Ti-6Al-4VAlloy

Electrophoretic deposition experiments were carried out at room temperature of 30 °C by setting a constant voltage of 30 V and the deposition was performed for 10 min. Ti-6Al-4V alloy was used as the cathode and platinum electrode was used as the anode. The distance between the two electrodes was 3 cm. These conditions were obtained by an optimization process to attain deposits of satisfying thickness and uniformity. Finally, the samples were dried in air for 24 h and stored in a desiccatorat room temperature.

2.5 SurfaceCharacterization

Fourier transform infrared (FTIR) spectra of the composite were recorded on a Nicolet 380 FTIR spectrometer (PerkinElmer) over the frequency range from 4000 to 400 cm^{-1} with 32 scans and spectral resolution of 4 cm^{-1}. The surface morphology and elementalcomposition

of the composite coatings were examined by scanning electron microscopy (SEM) analysis and Energy dispersive X-ray analysis (EDAX) (JEOLJSM-6400).

2.6 Electrochemical Evaluation of CompositeCoatings

Electrochemical measurements were carried out through potentiodynamic polarization to assess the anticorrosive characteristics of the coatings. A saturated calomel electrode (SCE), platinum electrode, and Ti-6Al-4V alloy were used as the reference, counter, and working electrode, respectively. Simulated body fluid (SBF) solution with ion concentration nearly equal to that of human blood plasma was used as electrolyte medium. This solution was prepared according to the protocol suggested by Kokubo and Takafama[6]. Potentio dynamic polarization studies were measure data scanrate of $1mV \cdot s^{-1}$ in the potential range between-1 and 1V vs SCE. The obtained data was recorded by use of internally available software.

3. Results and Discussion

3.1 FTIRAnalysis

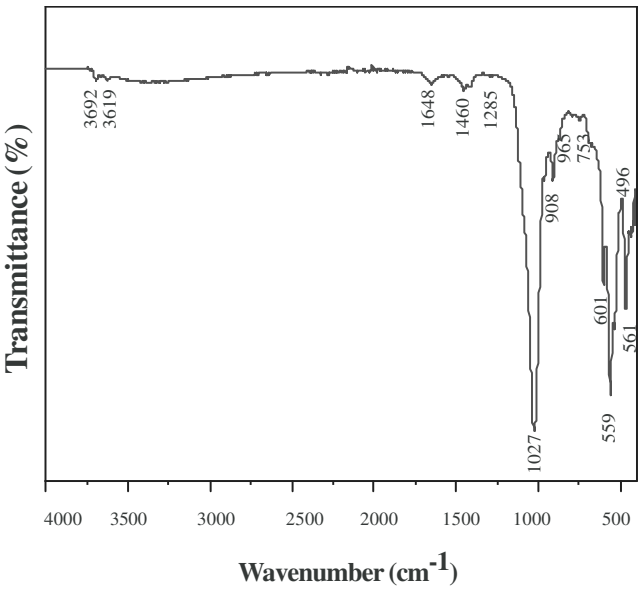


Figure 1: FTIR Analysis of HAP/HNT/PVP composite

Figure 1 shows the FTIR spectrum of HAP/HNT/PVP composite coated Ti-6Al-4V alloy. The absorption bands at 3692 and 3618 cm^{-1} are attributed to –OH groups on the internal surface of the HNT. The peak at 1027 corresponds to perpendicular Si–O stretching and stretching bond of P-O groups. The peak at 908 cm^{-1} is due to the O-H deformation vibration of inner Al-OH groups (between the interface of the Al-O octahedron and the Si-O tetrahedron) present in HNT[4]. The characteristic peaks of C=O stretching vibration can be observed at 1648 cm^{-1} which denotes the addition of PVP. The bands at 753, 865 and 1285 cm^{-1} are attributed to C-C stretching, C-N stretching and C-H bending vibrations of the PVP respectively[8]. The characteristic peaks appeared at 908 $cm^{"1}$, 593 $cm^{"1}$, 559 $cm^{"1}$, and 461 $cm^{"1}$, and the band observed at 945 $cm^{"1}$ depicts the phosphate groups[7]. Hence, the peaks are evident for the formation of HAP/HNT/PVPcomposite.

3.2 SEM/EDAXAnalysis

The SEM images provide direct information about the typical morphology of the HAP/HNT coated and HAP/HNT/PVP specimens (Figure 2). The SEM images of HAP/HNT (Fig.2(a & aÈ)) coated Ti-6Al-4V revealed the presence of rod-like structure

with micropores formed between those structures with certain level of agglomeration of HNT[5]. Fig.2b & 2bÈ shows that the surface is entirely covered with the uniform and continuous coating with crack free micropores[7]. Hence the HAP/HNT/PVP composite coating can be an potential obstruction on Ti-6Al-4V and may be give corrosionprotection.

The EDAX spectrum representing the constituent elements of the HAP/HNT/PVP coating on Ti-6Al-4V is shown in Fig. 2(c).The spectrum shows the presence of Ca, P, O, Si, Al, C and N. This result reveals the existence of HAP, HNT, and PVP in the composite.

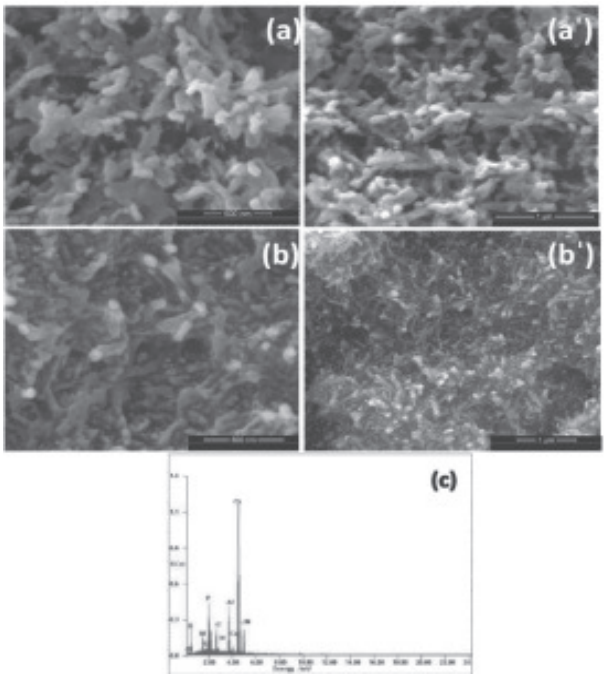


Figure 2: SEM micrographs of (a, aÈ) HAP/HNT, (b, b') HAP/HNT/PVP coatings

1.1 Potentiodynamic polarisation studies

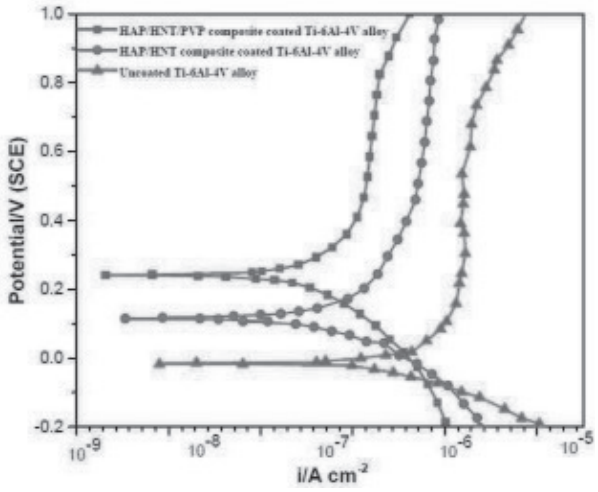


Figure 3: Potentiodynamic polarization curves for uncoated, HAP/HNT and HAP/HNT/PVP coated Ti-6Al-4V alloy

In order to examine the corrosion protection performance of the as-formed coatings in SBF solution for long term applications, the typical potentiodynamic polarization study was carried out. The potentiodynamic polarization curves of the uncoated Ti-6Al-4V, HAP/HNT, and HAP/HNT/PVP composite coated Ti-6Al-4V, respectively in SBF were obtained in the potential range of -1V to 1V vs. SCE. The corresponding polarization plots are shown in Fig.

3. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values for uncoated and coated samples were observed and are summarized in Table 1.

As inferred from the table, the HAP/HNT coated Ti-6Al-4V alloy showed more positive E_{corr} and

Table 1: Electrochemical parameters and Hardness values of uncoated, HAP/HNT coated and HAP/HNT/PVP coated Ti-6Al-4V alloy

SAMPLE	E_{corr} (mV)	i_{corr} (µA.cm^{-2})
Uncoated Ti-6Al-4V alloy	-12 ± 0.5	1.29 ± 0.04
HAP/HNT coated Ti-6Al-4V alloy	115 ± 0.10	0.87 ± 0.07
HAP/HNT/PVP coated Ti-6Al-4V alloy	235 ± 0.08	0.49 ± 0.06

much lower i_{corr} compared to the uncoated Ti-6Al-4V alloy, whereas the HAP/HNT/PVP composite coating on Ti-6Al-4V alloy strengthened the corrosion resistance. Thus, potentiodynamic polarization studies denotes that the corrosion resistance of the Ti-6Al-4V alloy was significantly improved due to the HAP/HNT/PVP composite coating.

4. Conclusions

Fabrication of HAP/HNT/PVP on Ti-6Al-4V alloy was successfully performed by electrophoretic deposition. The FT-IR analysis confirmed the formation of HAP/HNT/PVP composite. Morphological results revealed the formation of composite coatings with uniform and crack free morphology which denotes the protection of the Ti-6Al-4V alloy as implants. The corrosion resistance of HAP/HNT/PVP coated Ti-6Al-4V alloy assured the improved corrosion protection in SBF solution. Hence, the developed HAP/HNT/PVP coated Ti-6Al- 4V alloy can be a more potential candidate in orthopedic applications

5. References

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