Dip Coating of Hydroxyapatite, PCL and Gelatin Composites on Metallic Implant for Biomedical Applications

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Abstract. Titanium and its alloys have found application in biomedical fields primarily because of their sterling mechanical characteristics and bio-compatibility. But they can corrode when in contact with body fluids thereby being a limitation to their longevity. This is why surface modification techniques play a crucial role in strengthening the protection of the material and rendering it corrosion resistant. In this study, composite of HA/PCL/Gelatin was successfully deposited on Ti6Al4V substrate by dip coating technique. Microscopic analysis showed that the 70% PCL coating resulted in a smoother and more uniform surface compared to the 30% PCL coating. Rockwell C hardness testing confirmed that the Ti-6Al-4V substrate had a hardness of 35 HRC. Scotch tape adhesion tests indicated superior bonding strength for the 70% PCL coating, with minimal coating removal. In Ringer's solution, the 70% PCL coating exhibited only 11% degradation over three weeks, while the 30% PCL coating showed 29% degradation. These results demonstrated that higher PCL content significantly enhances coating adhesion and corrosion resistance, suggesting improved long-term stability and performance of Ti implants.

Keywords: Bioactive materials, medical Implants, dip coating, Corrosion protection

1 Introduction

Orthopedic and dental implants made out of Titanium (Ti) and its alloys are very popular, largely because of their high mechanical strength and resistance to corrosion in physiological solutions [1, 8]. However, a critical challenge is for long-term implant stability; this is due to a phenomenon known as corrosion [2, 9]. Ti implants interact with body fluids and as a result of this interaction, the surface of the implant deteriorates and releases metal ions into the surrounding tissue, which in turn can cause adverse reactions to the surrounding tissue resulting to failure of the implant [1, 7, 10].

This paper aims to address these challenges and improve implant performance, there is an increasing focus on the development of bioactive coatings. Hydroxyapatite (HA), a calcium phosphate with a composition similar to natural bone, is widely used due to its

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ability to promote bone formation and integrate with bone tissue [3]. Additionally, Polycaprolactone (PCL), a biodegradable polymer known for its mechanical strength and biocompatibility, can be combined with HA to enhance coating properties [3, 13]. Gelatin, a natural polymer with adhesive properties, further complements these coatings by improving their adhesion and biocompatibility [9]. As PCL lacks surface wettability and functional surface groups that improve surface attachments [3], two polymers, PCL and gelatin, are incorporated to overcome this limitation [4]. The reason incorporating HA to the polymers is to enhance the bonding strength of the coating [3, 5, 14].

In this study, we aim to develop and evaluate a bioactive coating composed of HA, PCL, and gelatin applied to titanium alloy (Ti6Al4V) using the dip coating technique. This technique is chosen for its simplicity and effectiveness in creating uniform coatings [3]. The method of dip-coating has a great number of benefits for applying this composite coating. Dip-coating has the capability of applying coating on geometrically intricate implants at relatively low temperatures hence avoiding heat induced damage on the Ti substrate. [3, 12]

To determine the efficiency of the coating procedure, a comprehensive set of characterization methods was employed [4]. Fourier-Transform Infrared Spectroscopy (FTIR) was used to identify the presence and composition of the coating materials. Microscopic analysis was conducted to evaluate the coating morphology. The Rockwell hardness test measured the mechanical properties of the coating, while the Scotch tape test assessed its adhesion strength. Additionally, Ringer's solution testing was performed to mimic physiological conditions and evaluate the corrosion resistance of the coating [4].

2 Materials and methods

2.1 Synthesis of hydroxyapatite (HA)

Calcium nitrate tetra hydrate [Ca(NO3)2.4H2O] and diammonium hydrogen phosphate [(NH4)2HPO4] are used to prepare the hydroxyapatite.

10Ca (NO3)2 +6(NH4)2 HPO4+2NH4OH → Ca10 (PO4)6(OH)2 +14NH3+10H2O+20NO2 (1)

Hydroxyapatite was synthesized using microwave assisted co-precipitation method. Calcium nitrate tetra hydrate [Ca(NO3)2.4H2O] from BDH Laboratory (Bh15 1TD)) and diammonium hydrogen phosphate [(NH4)2HPO4] from Sigma Aldrich (MFCD00010891)) were selected as Ca and P precursor. 1 molar solution of Calcium Nitrate tetra hydrate and 0.6 molar solution of diammonium hydrogen Phosphate was prepared separately by mixing 94.56g Calcium Nitrate tetra hydrate and 31.7g of diammonium hydrogen Phosphate in 400ml distilled water, on magnetic stirrer and pH was maintained at 10 by adding NH3 from Merck (B756526). Diammonium hydrogen Phosphate was then added to the calcium nitrate tetra hydrate solution in a drop-wise manner with the help of dropping funnel. pH was maintained above 10. After maintaining pH, filtration process was started. Precipitate obtained was washed three times using distilled water until the pH dropped to 7. The residue of the filtration was spread on another filter paper. Then, it was placed at 80ºC for 24 hours in hot air oven. HA was dried and then ground well into a powder using a porcelain mortar and pestle. After that HA was kept in muffle furnace for 3 hours at 900 ºC for heat treatment [6].

2.2 Preparation of HA/PCL/Gelatin slurry

Two slurries were prepared having different concentration of reagents. One slurry was made with 70 wt. % of PCL and 30 wt. % of HA while other slurry consist of 70 wt. % of HA and 30 wt. % of PCL. The amount of gelatin was kept constant in both slurries.

At first, PCL-HA suspension was prepared. To prepare the suspension, PCL pellets were dissolved in chloroform (Sigma Aldrich) at 60 degrees Celsius. After complete dissolution of PCL pellets corresponding amount of HA was added and the resultant mixture was stirrer on magnetic stirrer for some hours. HA-PCL suspension was ready. After that 10 wt. % gelatin solution was prepared separately in distilled water at temperature between 55 – 60 degrees Celsius. Solution of gelatin was added in slurry in drop wise while keeping the suspension on stirrer. The mixture was stirred for some hours in order to obtain a homogenous slurry suitable for coating.

Both slurries were prepared using same method described above. The only difference was the amount of PCL and HA added.

2.3 Deposition of HA/PCL/Gelatin composite onto Ti6ALV4

Ti6Al4V plate was used as the metallic substrate. Before deposition, the surfaces of the substrate were mechanically cleaned with 1000 grit-sized SiC papers and then dipped in acetone and dried.

The cleaned plates were dipped in the PCL/HA/Gelatin suspension and then withdrawn. After that plates were dried at room temperature. Finally the coated substrate was characterized to study its mechanical and chemical properties.

2.4 Characterization of HA/PCL/Gelatin composite coating

The surface analysis of the coating was done by using microscope (Euromax). To evaluate the smoothness and to analyze the surface, a plate having deposited layer of composite was observed on microscope. The functional groups of HA and HA-PCL-Gelatin composite was identified by using FTIR. FTIR spectra were recorded in the region of 400–4000 cm−1 with scan rate of 4 cm−1 averaging over 128 scans. To determine the coating adhesion to Ti alloy plate, the pull-off test was carried out. The scotch tape was applied and removed to observe the adhesion strength. Rockwell hardness testing was done to assess the mechanical strength of Ti alloy plate. The test ensures that the material is strong enough to withstand possible mechanical stress if occur. The corrosion behavior of coated plate was studied using Ringer testing. Coated plates were placed in ringer solution at 37 degrees Celsius. Plates were observed over the period of 3 weeks.

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3 Results and discussion

3.1 FTIR testing

The FTIR spectrum of hydroxyapatite below (HA) shows significant peaks including the O-H stretching mode at 3728 cm^{-1}, which indicates the crystalline nature of HA due to the short, strained O-H bonds. The P-O stretching peaks appear at 1045 and 967 cm^{-1}, reflecting longer P-O bonds in the sample. The peak at 643 cm^{-1}, associated with the librational mode of the hydroxyl group, further confirms HA's crystallinity. The bending mode of the O-P-O linkage is observed at 578 cm^{-1}. Bending vibrations of the PO_4 group are seen in the 578-610 cm^{-1} range. These peaks demonstrate that the sample contains hydroxyl (O-H) and phosphate (PO_4) groups, providing a comprehensive understanding of HA's molecular properties Fig 1.

3.1.1 FTIR of HA

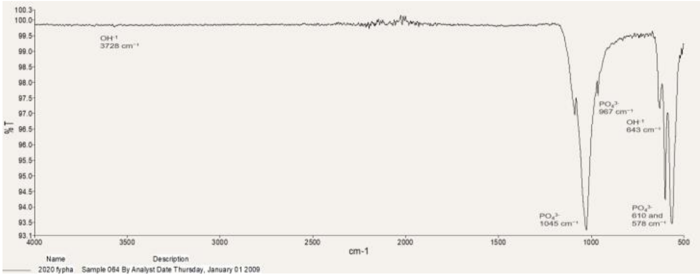


Fig.1. FTIR analysis of HA

3.1.2 FTIR of Composite

The FTIR spectrum compares two samples with different concentrations of polycaprolactone (PCL) and hydroxyapatite (HA). The black line represents a coating with 70% PCL, 30% HA, and 0.5g gelatin, while the blue line shows a higher concentration of HA at 30% PCL, 70% HA, and 0.5g gelatin. The broad peak centered around 3384 cm-1 in both spectra is characteristic of the O-H stretching vibration, predominantly contributed by the hydroxyl groups within the HA component. The presence of aliphatic structures, primarily from PCL, is evident in the multiple peaks within the 2869-2952 cm-1 region, corresponding to C-H stretching vibrations. Sample 2 it is more pronounced because of higher concentration of PCL in sample 2.

A prominent peak at 1763 cm-1 in both spectra is attributed to the carbonyl stretching vibration of the ester functional group, characteristic of PCL. However, its relative intensity is more pronounced in sample 2 due to its higher PCL content. The region around 1628 cm-1 encompasses the amide I band, primarily associated with C=O stretching vibrations of the amide groups in HA and gelatin. The CH_2 bending vibrations, primarily originating from PCL, contribute to the peak observed at 1402 cm-1. While this peak is present in both spectra, it is more prominent in sample 2 due to its higher PCL concentration.

Additionally, a peak around 1048 cm-1, potentially indicative of P-O stretching vibrations, suggests the presence of phosphate groups, originating from HA.

Overall, the FTIR analysis confirms that Sample 1 is more HA-rich, with dominant phosphate peaks, while Sample 2 is more PCL-rich, showing more prominent aliphatic (CH_2) and carbonyl (C=O) peaks. This spectral analysis highlights the compositional differences between the two coatings and their corresponding vibrational modes Fig 2.

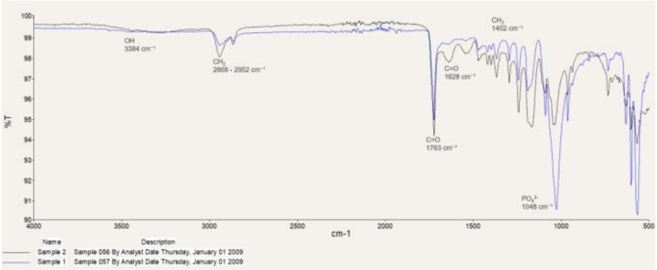


Fig.2. FTIR analysis of sample 1(30%PCL/70%HA/0.5g gelatin) and Sample 2 (70%PCL/30%HA/0.5g gelatin)

3.2 Hardness testing

The Rockwell C scale (HRC) hardness test with a diamond indenter was employed to assess the mechanical strength of the bare titanium alloy substrate (Ti-6Al-4V), commonly used in orthopedic implants. The Ti alloy exhibited a hardness value of 35 HRC with a standard deviation of 0.87 HRC, confirming its suitability for orthopedic applications due to its strength and ductility. The test was conducted with a standard load of 150 kgf, at room temperature and under standard laboratory conditions. The surface of the titanium plates was sanded with sandpaper to ensure a smooth finish. The slight variation from the literature value of approximately 36 HRC can be attributed to sample preparation

3.3 Surface analysis of the coated plates

Microscopic analysis of the composite coatings reveals a clear influence of PCL content on surface morphology. The 70% PCL/HA/gelatin coating Fig 3(a) exhibits a smoother and more uniform surface, while the 30% PCL/HA/gelatin coating Fig 3(b) appears rougher and more porous. This suggests that a higher PCL content leads to a denser overall coating structure with the formation of more beneficial surface-level pores. These pores promote osseointegration. Both coatings have crack-free structure is crucial to prevent corrosion of the underlying titanium substrate [3].

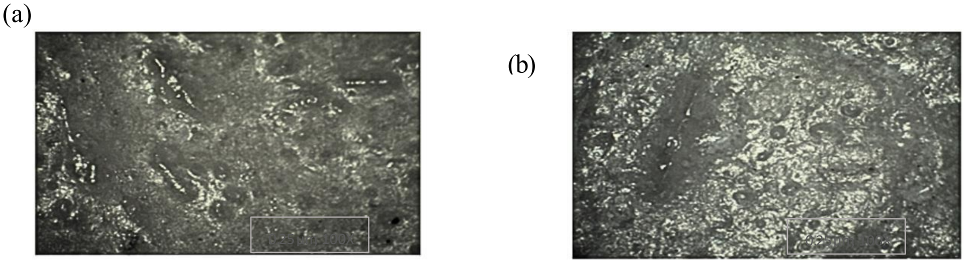
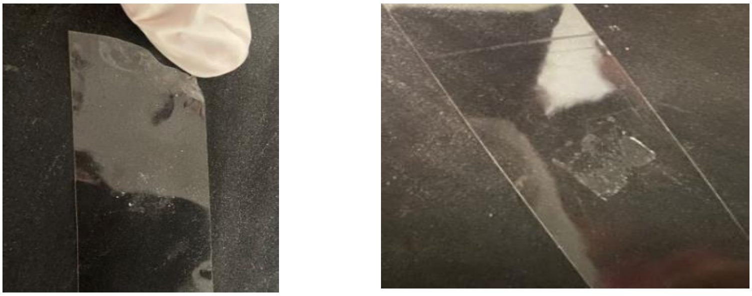


Fig. 3 (a) Microscopic images of titanium plates coated 70% PCL, HA and gelatin **(b)** Microscopic images of titanium plates coated with 70% HA, PCL and gelatin

3.4 Adhesion test using scotch tape

The Scotch tape adhesion test was used to assess the bonding strength of coatings on the plates. By applying and removing Scotch tape from the coated surfaces, we measured the amount of coating that transferred to the tape. This test effectively indicates the coating's adhesion quality, as a high adhesion level signifies strong bonding, which is crucial for the coating's durability and performance. The plate coated with 70% PCL, HA, and gelatin demonstrated exceptional adhesion, with nearly 3-4% coating coming off on the tape, indicating strong bonding as shown in fig 4(a). Conversely, the plate coated with 30% PCL, HA, and gelatin showed 10% removal of coating, with some of it adhering to the tape fig 4(b).



a. b.

Fig. 4(a) scotch tape testing of plate with 70%HA, PCL and gelatin **(b)** scotch tape testing of plate with 30%PCL, HA and gelatin

3.5 Study of corrosion behavior Ringer solution testing

Ringer's solution is a solution containing several salts and ions which are dissolved in water to creating an isotonic solution in order to mimic the internal environment of the human body. The composition of ringer solution is NaCL(6.43gL-1), KCL(0.19gL-1), CaCL(0.27gL-1), C8H18N2O4S (Hepes buffer) (2.38gL1), Glucose (C6H12O6) (1.80gL-1) [7], Ringer test was performed in order to assess the degradation of coated plates when placed in a solution which mimics the body-like environment. Two beakers half filled with ringer solution is taken and both coated plates (having 70% PCL and 30% PCL) were placed separately in ringer solution beakers at 37°C and were observed for 3 weeks. The initial weight of plate without coating was also measured. The percentage of coating removed from the plates after 1st, 2nd and 3rd week was noted by weighing the plates to observe its degradation rate.

After observing the plate for 3 weeks, it was noted that approximately 29% of the coating was removed over the period of 3 weeks from the plate containing 30% PCL. Meanwhile, the plate containing greater amount of PCL (70%) shows slower degradation with only 11% % of the coating removed over 3 weeks. This shows that coated plate with a higher amount of PCL degrade much slowly than the plate having less amount of PCL. This means the later plate can provide better corrosion resistance and last long.

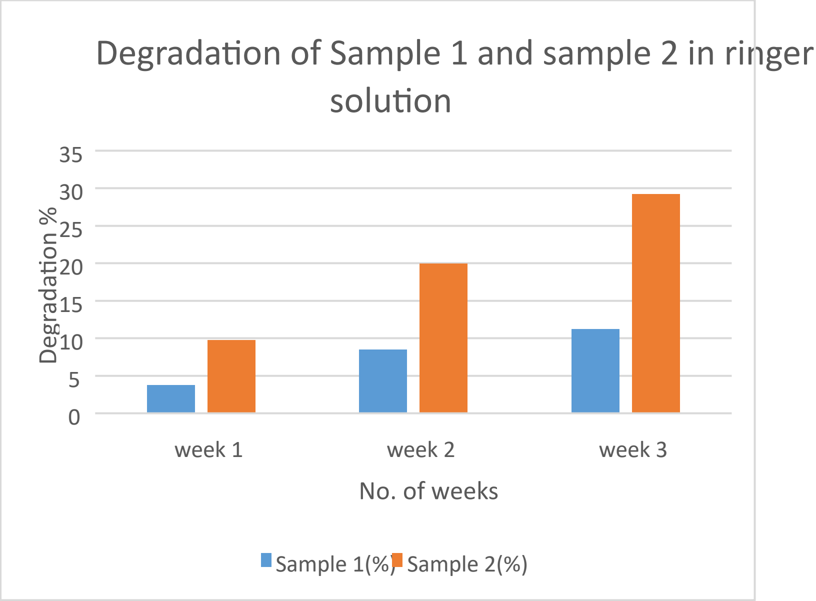


Fig.5 (Sample 1) Percentage of coating removed from the plates (70% PCL) over the period of 3 weeks**. (Sample 2)** Percentage of coating removed from the plates (30% PCL) over the period of 3 weeks

Microscopic analysis of the coated plates after immersion in ringer solution revealed that 70% PCL coating (Fig 3.5(a)) exhibited strong adherence even after three weeks of Ringer's solution testing, with no observed peeling when compared to their before pictures. This suggests good corrosion resistance. Conversely, the 70% HA coating (Fig. 5(b)) displayed a coarse and loosely packed surface with exposed titanium regions after immersion in ringer solution for 3 weeks. Notably, this coating became even more loosely packed after Ringer's solution exposure.

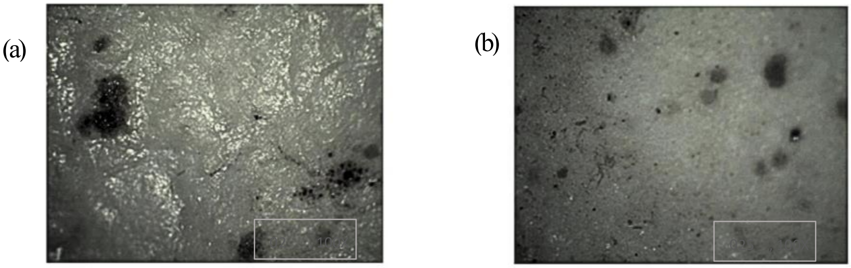


Fig 6 (a) Microscopic images of titanium plates coated 70% PCL, HA and gelatin in ringer solution **(b)** Microscopic images of titanium plates coated with 70% HA, PCL and gelatin in ringer solution

4 Conclusion

In conclusion, the study demonstrated that the composite coating with 70% polycaprolactone (PCL) exhibited superior properties compared to the 30% PCL coating. The 70% PCL coating provided a smoother, more uniform surface, better adhesion as evidenced by the Scotch tape test, and greater corrosion resistance, with only 11% degradation in Ringer solution over three weeks. These characteristics suggest that a higher PCL content enhances the coating's durability and effectiveness in protecting titanium-based orthopedic implants, while the FTIR analysis confirmed the presence of crucial functional groups in both coatings, validating their composition and potential application in biomedical fields.

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