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# Characterization of Chitosan Polyethylene glycol Hydroxyapatite composite coatings fabricated by dip coating

# Caracterización de recubrimientos compuestos de quitosano polietilenglicol hidroxiapatita fabricados por dip coating

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**Abstract**

The development and characterization of bioactive surfaces based on chitosan-polyethylene glycol coatings modified with hydroxyapatite on Ti6Al4V alloy were conducted to enhance bioactivity. Characterization techniques such as scanning electron microscopy, X-ray diffraction, infrared spectroscopy, atomic absorption spectroscopy, and electrochemical impedance spectroscopy were used to evaluate coating properties, apatite formation after immersion in simulated body fluid, and electrochemical stability. Results demonstrated apatite deposition due to the bioactivity of the polymer-ceramic composite, with calcium accumulation observed on the substrate surface after 5 days of immersion. Electrochemical impedance spectroscopy revealed a highly capacitive layer in the 50:50 chitosan-polyethylene glycol coating with 0.05% w/v hydroxyapatite, indicating increased interaction with the biological medium while preserving the protective resistive properties of the Ti6Al4V alloy. These findings suggest that this coating composition is a promising material for bone tissue regeneration applications.

**Keywords:** Ti6Al4V alloy; surface modification; alkaline treatment; polymer-ceramic coatings; bioactive coatings; simulated body fluid; calcium absorption; apatite formation; electrochemical behavior; surface engineering; bone regeneration.

**Resumen**

Se desarrollaron y caracterizaron superficies bioactivas basadas en recubrimientos de quitosano-polietilenglicol modificados con hidroxiapatita sobre aleación de Ti6Al4V, con el objetivo de mejorar su bioactividad. Se emplearon técnicas de caracterización como microscopía electrónica de barrido, difracción de rayos X, espectroscopía de infrarrojo, absorción atómica y espectroscopía de impedancia electroquímica para evaluar las propiedades de los recubrimientos, la formación de apatitas tras la inmersión en fluido fisiológico simulado y la estabilidad

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electroquímica. Los resultados demostraron la deposición de apatitas debido a la bioactividad del compuesto polímero-cerámico, con acumulación de calcio en la superficie del sustrato tras 5 días de inmersión. La espectroscopía de impedancia electroquímica reveló una capa altamente capacitiva en el recubrimiento con proporción 50:50 de quitosano: polietilenglicol y 0.05% p/v de hidroxiapatita, indicando una mayor interacción con el medio biológico, al tiempo que preservaba las propiedades resistivas protectoras de la aleación Ti6Al4V. Estos hallazgos sugieren que esta composición de recubrimiento es un material prometedor para aplicaciones en regeneración de tejido óseo.

**Palabras clave:** Aleación Ti6Al4V; modificación superficial; tratamiento alcalino; recubrimientos polímero-cerámicos; recubrimientos bioactivos; fluido corporal simulado (SBF); absorción de calcio; formación de apatita; comportamiento electroquímico; regeneración ósea.

## 1. Introduction

Biomaterials have played a highly important role in the design of biomedical devices and the development of tissue engineering [1], [2], [3]. This has led to the opening of a new and very varied field of action in the research and development of surfaces with regenerative properties. The main requirement for biomaterials is that they are biocompatible and resistant to any alteration in their surface and structure when implanted [4], [5],[6].

Some of the most widely used materials in tissue engineering today are metals and their alloys [7], [8], [9]. These have played a predominant role as structural biomaterials in reconstructive surgery, especially in orthopedics, with more recent uses in non-bone tissues, such as vascular stents.

Titanium and its alloy Ti6Al4V ELI stand out among metallic biomaterials due to their wide use as orthopedic and dental implant materials. The surfaces of these materials have a combination of properties that have allowed them to position themselves as the best alternatives on the market for this type of application [10], [11],[12], [13].

However, the titanium oxide (TiO2) layer that protects the surface of titanium and its alloys makes them chemically inert materials, so it has become necessary to implement surface modification techniques to create these surfaces bioactive materials [14] and biofunctional [15].

Some studies that have been carried out to improve the biological response of the Ti6Al4V ELI titanium alloy surfaces have focused on chemical treatments. [16], oxidation process [17], [18], [19], coating deposition [20], [21], [22], laser surface modification [23], [24] among many others. These efforts have allowed us to advance in understanding the material's biological response when implanted. However, there is still much to do in this field.

Various studies have focused on analyzing the effect of the surface on the mineralization processes and the cellular response of the implant material [25], [26]. Some works on implementing polymers demonstrate that polyethylene glycol (PEG) is a promising material in bone regeneration applications [27]. Studies have explored PEG-based hydrogels as carriers of osteogenic substances, improving bone healing [28]. PEG, in combination with biphasic calcium phosphate (BCP) scaffolds and mesenchymal stem cells, has facilitated bone regeneration in critical size defects [29]. Furthermore, PEG-based composites with decellularized bone extracellular matrix have shown increased hydrophilicity, cell viability, and osteoinductive properties, making them promising for tissue regeneration [30].

In addition to PEG, hydroxyapatite (HAp), a naturally occurring calcium phosphate, stands out as a key material in biomedical applications due to its chemical similarity to the mineral component of bone. This similarity grants HAp exceptional bioactivity, facilitating its direct bonding with native bone tissue. Studies have demonstrated that hydroxyapatite enhances osteoconduction, promoting the growth of new bone on its surface, and supports osteointegration when used as a coating material on metallic implants. Furthermore, HAp-based composites have been explored for their ability to improve the mechanical compatibility of biomaterials with bone, mitigating issues related to stress shielding, making HAp a pivotal component in developing bioactive surfaces for orthopedic and dental applications [31], [32].

Likewise, chitosan, a natural biopolymer, shows promise in bone tissue engineering [33], [34], [35]. Incorporating chitosan in scaffolds with other materials, such as gel and hydroxyapatite carbonate, can promote the proliferation and differentiation of osteoblasts, which is crucial for bone regeneration [36]. The biocompatibility of chitosan, PEG and HAp and their ability to induce cell differentiation make them valuable materials for bone regeneration applications.

The present study contributes significantly to the scientific community by developing bioactive coatings that enhance the bioactivity of Ti6Al4V alloys. These coatings provide a scalable and cost-effective approach to improving surface interaction with biological environments, addressing the bio-inertness of titanium and its alloys. Additionally, using biodegradable and biocompatible materials such as chitosan and polyethylene glycol reduces the environmental impact of biomaterial production. These advancements reinforce the potential of chitosan: PEG-Hap composites as innovative materials for regenerative medicine and biomedical implants.

For this reason, in this work, we study the in vitro response of chitosan, polyethylene glycol, and hydroxyapatite surfaces deposited on the Ti6Al4V Eli alloy using dip coating as a new proposal for composite materials for bone regeneration applications.

## 2. Materials and methods

In this section, we present a detailed description of the materials and methods used in this research, outlining the preparation process for the chitosan, polyethylene glycol, and hydroxyapatite composite coatings. The characterization techniques employed to evaluate the properties of the coatings are described, as well as the experimental conditions that ensure the validity of the results.

### 2.1. Materials

Polyethylene glycol with an average molecular weight of 8000, in powder form, chitosan derived from shrimp shells with a purity of ≥85% deacetylated, sodium hydroxide (NaOH), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, Nitric acid ($HNO_3$), Hydrofluoric acid (HF), sodium hydroxide (NaOH), acetic acid ($CH_3COOH$), ethanol were provided by Sigma-Aldrich, Merck. These included ACS. Quirúrgicos Especializados S.A. provided the titanium samples (ASTM F136 alloy) utilized.

### 2.2. Methods

The following methodology outlines a systematic approach to prepare and characterize composite coatings on Ti6Al4V substrates, integrating polymeric and ceramic components to enhance their bioactive properties. Each step was designed to ensure reproducibility and alignment with standards for evaluating biomaterial performance.

#### 2.2.1. Sample preparation

Ti6Al4V disc samples measuring 14 mm in diameter and 3 mm in thickness were utilized as substrates. The samples were mechanically grounded using silicon carbide paper in ascending grades from #120 to #1200 and polishing with alumina slurry with an average particle size of 3.0 µm and 0.05 µm. Then, the samples were cleaned ultrasonically using water for 5 minutes.

A chemical cleaning was also carried out; the samples were immersed for 5 minutes in an acid solution (10% HF + 45% $NHO_3$ + ultrapure water). Finally, the Ti6Al4V discs were rinsed with ultrapure water and degreased with ethanol in an ultrasonic bath for 5 minutes, then dried with hot air and stored in a desiccator until further use.

#### 2.2.2. Alkaline treatment

Subsequently, an alkaline treatment was conducted by immersing Ti6Al4V samples in a 10 M aqueous solution of NaOH at 60°C for 24 hours. Upon completion of the treatment, the samples were rinsed and dried for 24 hours at room temperature inside a desiccator [33]. Moreover, a heat treatment was carried out at 450 ºC for one hour to facilitate the formation of the disodium trioxotitanate ($Na_2TiO_3$) hydrogel layer, employing a heating rate of 10 ºC/s and slow cooling in the furnace to room temperature.

#### 2.2.3. Polymeric solutions

Solutions of 0.5 M acetic acid in distilled water were prepared. These solutions were employed as solvents to dilute the stoichiometric quantities of chitosan, with each solution being agitated until a homogeneous mixture was achieved. Subsequently, the necessary grams of polyethylene glycol (PEG) were added to obtain three solutions with chitosan: PEG ratios of 30:70, 50:50, and 70:30 w/w, respectively [37] (See Table 1).

Table 1. Chemical agents were necessary to prepare polymer solutions

| Chitosan (g) | Acetic acid (ml) | PEG (g) | Chitosan:PEG ratio |
|---|---|---|---|
| 0.1511 | 0.45 | 0.3503 | 30:70 |
| 0.2514 | 0.75 | 0.2538 | 50:50 |
| 0.3501 | 1.05 | 0.1541 | 70:30 |

#### 2.2.4. Hydroxyapatite synthesis

Hydroxyapatite was synthesized following the processes described by Montañez [38] (method 1), Pareja et al.,

[39] (method 2), and Guzman et al., [40] (method 3). Once the hydroxyapatite powders were obtained, they were analyzed using X-ray diffraction (XRD) to determine which method yields the highest amount of crystalline hydroxyapatite. After selecting the best synthesis method, the necessary amounts of ceramic to be added to the polymeric solutions to modify the surfaces of the Ti6Al4V alloy were calculated. The calculation presented in Table 2 allows for obtaining final solutions with a volume of 50 ml.

Table 2. Hydroxyapatite is necessary to prepare ceramic polymer coating mixtures

| Hydroxyapatite (%w/v) | Hydroxyapatite (g) |
|---|---|
| 0.01 | 0.0016 |
| 0.03 | 0.0048 |
| 0.05 | 0.0080 |

### 2.2.5. Coatings

The polymeric solutions were used to obtain a coating on the titanium alloy previously subjected to alkaline treatment through immersion and substrate extraction using the dip coating technique. The immersion and extraction velocity were set at 1.5 cm/s. The total immersion time was 10 s, followed by a drying period of 30 minutes at a temperature of 60°C, allowing for complete solvent evaporation (acetic acid and water). The process was repeated three times on each disc to produce three layers on the substrates. The prepared samples and their compositional characteristics are shown in Table 3

### 2.2.6. Apatite formation

To evaluate the apatite-forming capability, the coated Ti6Al4V discs were immersed in 30 ml of a simulated body fluid (SBF) solution [16] (see Table 4) for 120 hours in an incubator at 37 °C. At the end of the immersion test, aliquots were taken to analyze their calcium content using atomic absorption spectroscopy. The calcium standard sample was prepared from the SBF, and serial dilutions were made to obtain a calibration curve for comparison with the results obtained from each analyzed sample (see Figure 1).

### 2.2.7. Electrochemical characterization

Finally, using Electrochemical Impedance Spectroscopy (EIS), the material's behavior against degradation processes was successfully evaluated. For this purpose, a flat three-electrode cell was employed, where the coated Ti6Al4V samples were used as working electrodes, a high-purity graphite rod was used as the counter electrode, and Ag/AgCl (3 M KCl) was employed as the reference electrode. A 30 mVrms was applied, and a frequency sweep from 0.01 to 100000 Hz was conducted. The data were recorded using a Gamry 600 potentiostat, and the experiments were carried out at 37 ºC.

Table 3. Code assigned to each prepared sample

| Code | Chitosan:PEG ratio | Hydroxyapatite (%w/v) |
|---|---|---|
| C1 | 30:70 | 0.01 |
| C2 | | 0.03 |
| C3 | | 0.05 |
| C4 | 50:50 | 0.01 |
| C5 | | 0.03 |
| C6 | | 0.05 |
| C7 | 70:30 | 0.01 |
| C8 | | 0.03 |
| C9 | | 0.05 |

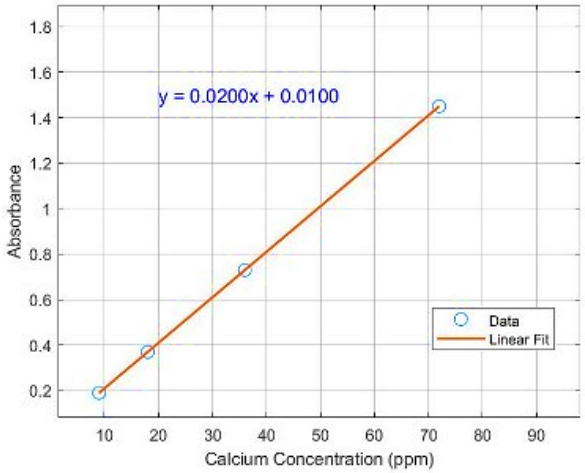


Figure 1. Calcium concentration calibration curve based on SBF dilution.

Table 4. Chemical composition of SBF solution

| Code | Hydroxyapatite (%w/v) |
|---|---|
| $Na^+$ | 0.01 |
| $K^+$ | 0.03 |
| $Mg^{2+}$ | 0.05 |
| $Ca^{2+}$ | 0.01 |
| $Cl^-$ | 0.03 |
| $HCO_3^-$ | 0.05 |
| $HPO_4^{2-}$ | 0.01 |
| $SO_4^{2-}$ | 0.03 |

Source:[16].

## 3. Results and discussion

The results obtained from the characterization tests conducted on the chitosan, polyethylene glycol, and hydroxyapatite composite coatings are presented below. The findings are discussed in detail, providing a clear view of how these coatings behave under simulated bodily environment conditions and their relevance for biomedical applications

Figure 2a shows the X-ray diffraction (XRD) patterns obtained from the hydroxyapatite powders synthesized by the three methods previously described (see section 2.2.4). The compositions of the powders, presented in Table 5, were determined experimentally through XRD analysis conducted in the laboratory. Diffractograms were processed and interpreted to quantify the crystalline phases in each sample, ensuring an accurate characterization of the synthesized materials.

Based on the analysis of the XRD results, method 2 (reported by Pareja et al. [39]) was selected for further use due to its ability to produce hydroxyapatite with a high degree of crystallinity (79% HAp), as well as the presence of other apatite phases that enhance its adsorption properties in biological environments.

Crystalline hydroxyapatite is widely recognized as superior to amorphous HAp in biomedical applications due to its improved stability, bioactivity, and osteoconductive properties. Its ordered structure facilitates direct bonding with bone tissue and promotes the formation of apatite layers in physiological environments, making it a more reliable candidate for bone regeneration. Additionally, crystalline HAp exhibits higher thermal and chemical stability, reducing the risk of degradation or phase transformation during processing and implantation, challenges often associated with amorphous HAp. These advantages make the hydroxyapatite synthesized using method 2 the most suitable choice for this study.

Figure 2b) presents an infrared spectrum characteristic of the nine recorded spectra (sample code C1). These spectra allowed for the identification of bonds between the functional groups of the polymeric blend through the vibrations of the atoms in the molecules. An important aspect to consider when comparing the different obtained IR spectra is the analyte concentration; although this does not generate notable changes in the spectra, it is indispensable to consider the Lambert-Beer law, which relates the analyte concentration to transmittance; in other words, an increase in peak intensity occurs with concentration.

Table 5. Chemical composition of Hap powders

| Method | Chemical composition |
|---|---|
| Method 1 (Montañez) | 57% Buchwaldite $Ca_{12}Na_{12}P_{12}O_{48}$ |
| | 25% Calcium oxide $Ca_4O_4$ |
| | 18% Fluorapatite $C_{10}P_6O_{24}$ $P_2$ |
| Method 2 (Pareja et. al.) | 79% HAp. $Ca_{10}P_6O_{28}$ |
| | 20% Whitlockite $Ca_{60.69}Mg_{2.31}P_{42}O_{148}$ |
| | 1% Calcium oxide $Ca_4O_4$ |
| Method 3 (Guzman et. al.) | 60% Calcium oxide $Ca_4O_4$ |
| | 27% Fluorapatite $C_{10}P_6O_{24}$ $P_2$ |
| | 13% HAp. $Ca_{10}P_6O_{28}$ |

Band assignments are presented in Table 6 and were carried out considering the interpretation tables of IR spectra and the results of authors such as [41], [42], [43], [44] and [45].

Table 6. Band assignments IR Spectrum

| Band ($cm^{-1}$) | Assignment | Ref. |
|---|---|---|
| 3263.14 | Primary amide N-H vibration associated with chitosan | [45] |
| 2861.50 | C-H vibration of chitosan | [45] |
| 1637.46 | Deformation of primary amide N-H associated with chitosan | [45] |
| 1238.98 - 1279.86 | C-O vibration of PEG | [43], [44] |
| 1104.79 | O-Ti-O vibration asymmetric stretching of $PO_4^{3-}$group | [41] |
| 1091.67 | C-O-C deformation of PEG | [43], [44] |
| 961.12 | Asymmetric vibration of $PO_4^{3-}$ group | [41] |
| 841.64 | Out pof plane C-H deformation of chitosan | [45] |
| 770.39 | Out of plane C-H deformation of the monosubstituted aromatic ring of chitosan | [45] |
| 468.68 | O-Al y $PO_4^{3-}$interaction | [41] |

Similarly, Figure 2c), Figure 2d), and Figure 2e) present the surface morphology of discs C3, C6, and C9, respectively. In these micrographs, it can be observed that the increase in chitosan concentration favors the coverage of the coating on the surface [37]. This can be appreciated by analyzing the decrease in areas of light gray tone that gradually disappear with the increase in chitosan concentration.

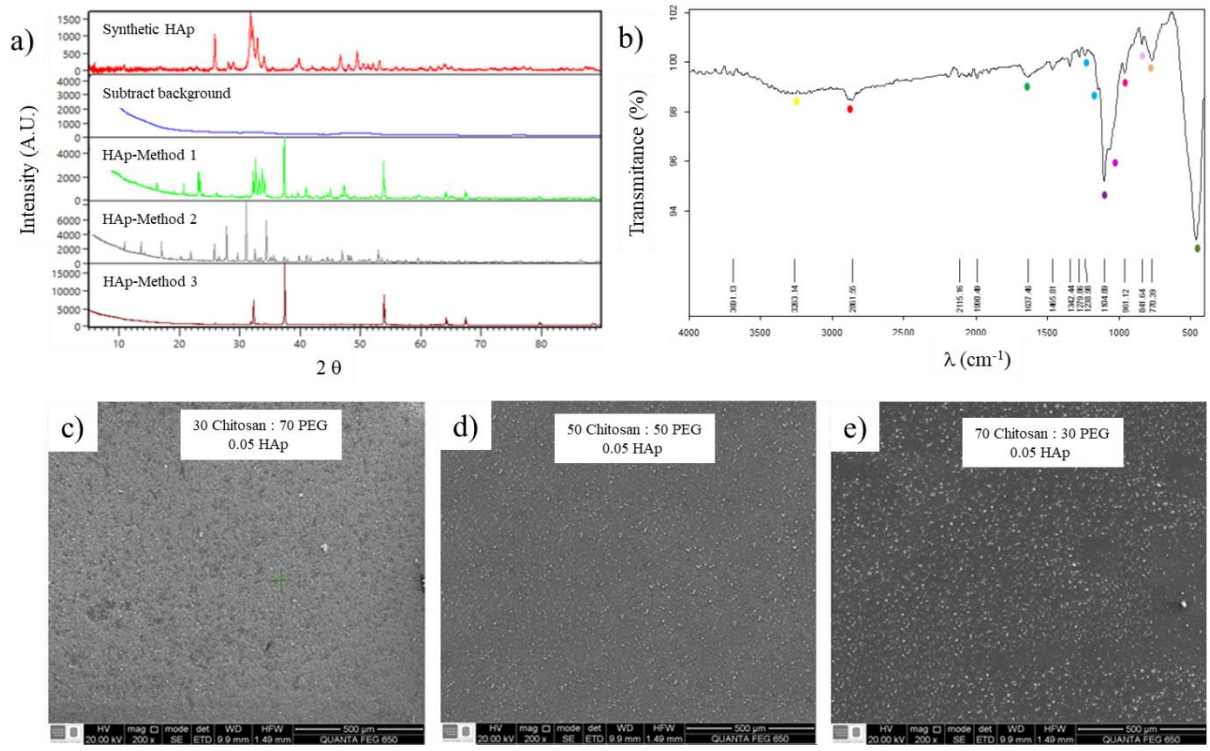


Figure 2. Surface characterization of chitosan: PEG - HAp coatings. a) DRX from the powders of Hydroxyapatite synthesized, b) FTIR spectrum from the surface C1 (30% chitosan-70% PEG and 0.01% HAp), and surface FESEM micrograph from c) C3 (30:70 Chitosan: PEG + 0.05 Hap), d) C6 (50:50 Chitosan: PEG + 0.05 Hap) and e) C9 (70:30 Chitosan: PEG + 0.05 Hap).

Additionally, more white clusters, which are associated with precipitates on the surface, can be observed. These clusters form because the HAp powders do not entirely dissolve when modifying the polymers with this ceramic material. Additionally, it can be observed that with the increase in chitosan concentration, a more homogeneous distribution of the clusters is observed.

On the other hand, in Figure 3a, Figure 3b, and Figure 3c, you can see the surfaces of the Ti6Al4V discs coated with the 50:50 ratio of chitosan: polyethylene glycol after the immersion test in SBF solution. These three surfaces presented the most significant amount of apatite agglomerates formed after the five days of the immersion test.

The increase in the concentration of HAp on the surface of the coating favors the formation of apatites; this is evident due to the rise in white agglomerates observed in these micrographs.

Instead, the Bode diagram curves (Figure 2e) show the electrochemical behavior for the 50:50 Chitosan: PEG ratio with different concentrations of HAp. In the high-frequency region, a highly capacitive coating (0.78 < CPE-P < 0.90) is associated with the polymeric films formed on the base alloy, which tend to interact easily with the SBF solution, achieving an exchange of ions. At low frequencies, a highly resistive behavior is observed (0.11 < CPE-P < 0.25) corresponding to the Ti6Al4V alloy. This interacts with the bioactive layer and prevents the deterioration of the alloy by the electrolyte.

Additionally, a behavior change is observed in the biomaterial, from capacitive to resistive, represented by the variation in the phase angle values and its drop when going from medium to high frequencies for the 50:50 ratio of Chitosan: PEG. For low-phase angles in the high-frequency range, the typical behavior of a porous surface is observed to allow the exchange of ions at the solution–coating interface.

From medium to low frequencies, there is an increase in phase angles associated with the change in the material's behavior (from resistive to capacitive). This behavior observed in the bode plot was fitted to the equivalent electrical circuit shown in Figure 2f. This circuit represents the general behavior of the coatings despite the

variation in the ceramic material (HAp). In the circuit, R1 corresponds to the solution resistance, SBF; CPE1 is the capacitance represented as a constant phase element associated with the electrochemical processes between the solution–coating interface; R2 is the resistance associated with the highly porous coating; CPE2 is the capacitance represented as a constant phase element associated with the coating–base alloy interface; and R3 is the resistance corresponding to the Ti6Al4V alloy [16], [33].

The findings presented in this study contribute significantly to the advancement of materials science and engineering by demonstrating a scalable and effective approach to developing bioactive surfaces for Ti6Al4V alloys. The coatings enhance surface interaction with biological environments, addressing the bioinert nature of titanium. From a technological perspective, the dip coating technique ensures material efficiency and reproducibility, making it feasible for industrial-scale production of biomedical implants. Environmentally, using biodegradable materials such as chitosan and polyethylene glycol minimizes waste generation during fabrication, aligning with sustainable development goals. These contributions reinforce the potential of chitosan: PEG-HAp composites for regenerative medicine, particularly in orthopedic and dental applications.

## 4. Conclusions

The coated surfaces' morphological, compositional, and structural characterization determined that the optimal polymer ratio was 50:50 Chitosan: PEG. Incorporating 0.05% w/v hydroxyapatite (HAp) into the coatings significantly enhanced their bioactivity, as evidenced by the increased formation of calcium phosphate agglomerates on the surface. The ability to form and precipitate apatite on the biomaterial's surface was quantitatively assessed using atomic absorption spectroscopy, which demonstrated that the 50:50 ratio of Chitosan: PEG with 0.05% w/v HAp exhibited the highest calcium absorption from the simulated body fluid. This behavior can be attributed to the high affinity of the ceramic component within the coating for the biological medium.

Electrochemical Impedance Spectroscopy (EIS) techniques allowed for the evaluation of the bioactivity and protective properties of the coatings. Two distinct behaviors were identified: a highly capacitive response in the high-frequency region, associated with bioactivity, and a highly resistive response in the low-frequency region, linked to the protective nature of the coating.

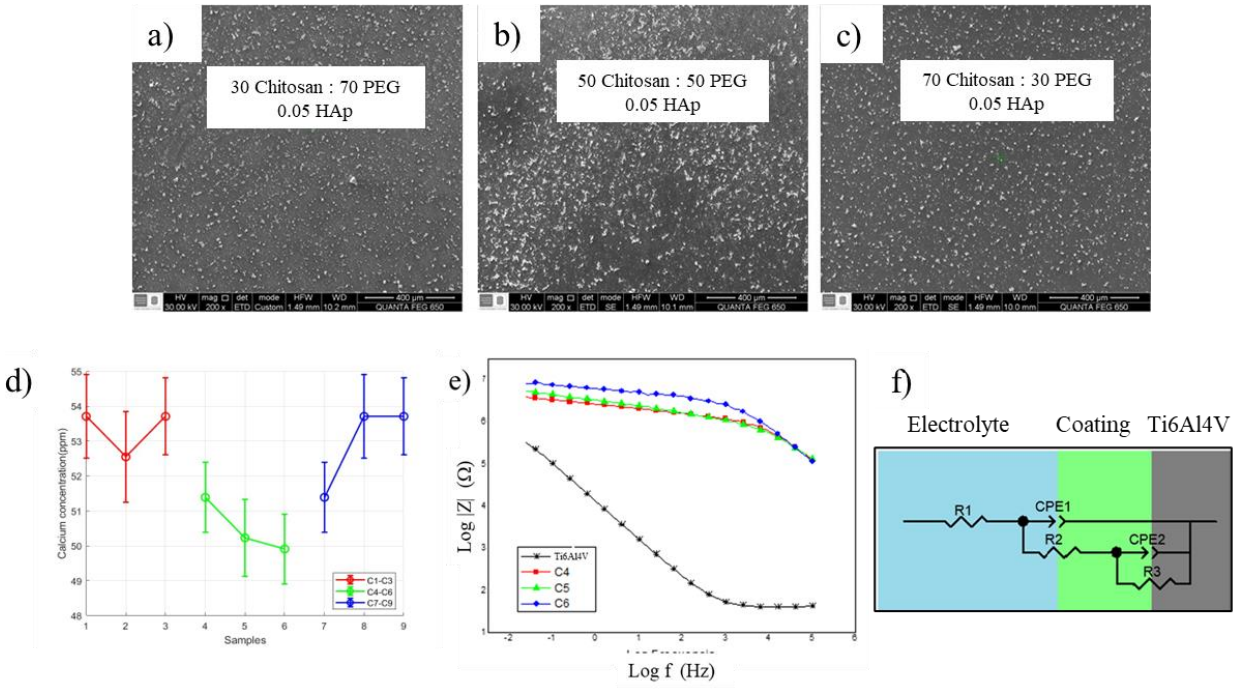


Figure 3. Surface characterization of chitosan: Polietilenglicol -Hydroxyapatite coatings. a) DRX from the three samples of Hydroxyapatite synthesized, b) FTIR spectrum from the surface C1 (30% chitosan-70% polyethyleneglycol and 0.01% hydroxyapatite), and surface FESEM micrograph from c) C3, d) C6 and e) C9.

The 50:50 polymer ratio of Chitosan: PEG with 0.05% w/v HAp demonstrated a higher polarization resistance (Rp) value compared to the base material, confirming its effectiveness in providing substrate protection while maintaining bioactive properties.

This study contributes significantly to the fields of biomaterials and biomedical engineering by offering a scalable and effective method to develop bioactive coatings for Ti6Al4V alloys. The findings demonstrate that the selected coatings not only enhance the bioactivity of the substrate but also provide improved surface interaction with simulated biological environments. The use of biodegradable and biocompatible materials, such as chitosan and polyethylene glycol, aligns with sustainable development goals by minimizing environmental impact during material production. Furthermore, the developed coatings have the potential to advance medical technologies by providing cost-effective solutions for orthopedic and dental applications, ultimately benefiting both the scientific community and society.

Future research could further optimize the chitosan: PEG-HAp coatings by exploring the incorporation of additional bioactive elements, such as magnesium or strontium, to enhance osteogenic and antibacterial properties. Additionally, in vitro and in vivo studies are necessary to validate the biocompatibility and long-term stability of the coatings in physiological environments. These efforts will help bridge the gap between laboratory findings and clinical applications, ensuring that these coatings meet the rigorous demands of modern regenerative medicine and implantology.

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## Autor Contributions

A. Sandoval-Amador: Conceived the original idea, conceptualization, validation, and writing and original draft. A. M. Nieto-Soto: Methodology, data acquisition, formal analysis, investigation. D. K. Díaz-Maldonado: Methodology, data acquisition, formal analysis, investigation. D. Y. Peña-Ballesteros: Supervision and editing. Hugo Estupiñán: Supervision and editing.

All authors have read and agreed to the published version of the manuscript.

## Conflicts of Interest

The authors reported no potential conflict of interest.

## Institutional Review Board Statement

Not applicable.

## Informed Consent Statement

Not applicable.

## Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

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