

Electrochemical Evaluation of a Semisynthetic Biocomposite Obtained from Rice Husk for Use as Bone Filler

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In this work, a biocomposite is obtained calcium phosphate and silica extracted from rice hulls in order to be used as bone filler, for cases where the patient has significant bone loss. Techniques of electrochemical impedance spectroscopy (EIS), Tafel curves and corrosion potential, to evaluate the surface electrochemically material was used when in contact with a physiological fluid (SBF). It was possible to obtain an impedance spectrum, which shows the phenomena of mass and charge exchange occurring on the surface of the material. With the use of electrochemical techniques other is set for each surface, the rate of degradation of material calcium phosphate and silica in concentrations 70-30 and 30-70% w / w respectively. Finally, through statistical analysis demonstrated the best performance by polarization resistance shown. The surface morphology was analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

1. Introduction

One of the most interesting ceramic used as bone filler is called bioglass or bioactive glass based silicon oxide mainly and also containing calcium, phosphorus and sodium (Shadjou and Hasanzadeh, 2015). This bioglass has an advantage over other well-known ceramic, hydroxyapatite, because it has two very important features in a biomaterial, such as the osteoconductive and osteoinductive, moreover, the bioglass faster way link with the host tissue (Naghizadeh et al., 2015). From 1971 (the year it was discovered the first bioglass 45S5), they have been tested many formulations, however it has been observed that biocompatibility properties are affected by the method of preparation (Catauro et al., 2015). Bioactivity bioglasses can be given by the presence of hydroxyl groups on the surface, which gives the nucleation ability calcium phosphate similar to bone concentrations, these reactions nucleation are followed by crystallization of apatite crystals, cell adhesion and formation of collagen (Ravarian et al., 2010).

Furthermore, calcium phosphate called hydroxyapatite is a material widely used in orthopedic devices, dental and as bone filler, because of their similarity in chemical composition to bone. It also has the feature is bioactive and osteoconductive (Padilla et al., 2006 and Farnoush et al., 2015). Calcium phosphates such as tricalcium phosphate (TCP) are considered absorbable, and have shown that as they degrade, they are replaced by host tissue (Ravarian et al., 2010). This research is aimed at the electrochemical evaluation and degradation rate of a semisynthetic biocomposite obtained by routes sol gel and aqueous precipitation, wherein the silicon oxide is extracted from a natural source as rice husk, while calcium phosphates are synthetic.

2. Methodology

2.1 Synthesis of semisynthetic biocomposite

The synthesis of crystals of calcium phosphate was performed by aqueous precipitation method, using the precursors calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and ammonium phosphate ($\text{H}_2(\text{PO}_4)\text{NH}_4$). The silica was extracted from rice husk by the sol gel method using hydrochloric acid and sodium hydroxide in the preparation of stable solution (Montañez and Peña, 2015). For obtaining the biocomposite, this was formed by

mixing calcium phosphates and silicon oxide in concentrations 70-30 and 30-70 % w / w respectively, after it was carried out heat treatment at 850 °C for two hours.

Before the electrochemical evaluation, the silicon oxide was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). The X-ray diffraction was carried out on a powder diffractometer (geometry DaVinci BRUKER D8 Advance, Germany), at a voltage of 40kV, current 30 mA, with internal standard corundum - alumina and sampling 0.02 °(2 θ). The fluorescence spectra of energy dispersive X-ray were obtained by the method of fundamental parameters using the DXP-700E software Version 1.00 Rel. 014, using a solid state detector Si (Li), 3 mm collimator and a tube of rhodium X-ray source. Finally electron microscopy was performed on a scanning electron microscope FEI Quanta 650 FEG, a detector EDAX APOLO X (resolution of 126.1 eV (Mn Ka)) for EDS analysis. Calcium phosphates were characterized by XRD.

2.2 Electrochemical characterization

Biocomposites are prepared in concentrations 70-30, and 30-70 % w / w calcium phosphate and silicon oxide, respectively. In a previous study, degradation of solid material in simulated physiological fluid was evaluated, finding that the material with the lowest percentage of degradation is composed of 70 % calcium phosphate – 30 % silica, with a percentage degradation of 0.19 % followed compound formed by the calcium phosphate 30 - 70 % silica, with a percentage of 0.47 %. The worst performance in terms of material degradation was 50-50 % w / w calcium phosphate - silicon oxide respectively with a percentage of 1.21 % in seven days (Montañez and Peña, 2015). Thus the electrochemical characterization was carried out in biocomposites 70-30 and 30-70 % w / w calcium phosphate - silicon oxide.

To evaluate material electrochemically, a disc of titanium (Ti6Al4V) alloy was coated by cathodic electrodeposition with semisynthetic biocomposite. Ti6Al4V samples were prepared surface with abrasive paper SiC number 600. Then the discs were washed with distilled water and ethanol in ultrasonic bath for 30 minutes. Electrodeposition was conducted at room temperature using a voltage source EC570-90 Thermo Electron Corporation, a time of 15 minutes, 20 Volts with agitation and with acetone as solvent.

An electrochemical cell of glass with flat tops of Teflon was used. Its dimensions were 40 mm in diameter and 40 mm length without caps, it has thread that fits perfectly into the bottom cover of Teflon and two glass capillaries Luggin. The sample is placed within the two bottom plates leaving an exhibition area of 0.785 cm² (Montañez, 2011). The parameters used for the impedance measurements were: from 100,000 to 0.01 Hz and 10 mV AC voltage. Before making the measurements of EIS, the corrosion potential was recorded for 300 seconds until the potential stabilized. The solution used for electrochemical measurements was SBF (Kokubo and Takadama, 2006), the cell was placed in an incubator maintained at 37 °C and is connected to Gamry potentiostat 600.

3. Results and discussion

3.1 Chemical characterization

The X-ray diffraction for oxide silicon evidenced that material was completely amorphous, with a signal of very low intensity at 21.86 ° 2 θ that was not assigned to any crystalline phase with a broadband (Montañez and Peña, 2015). In Figure 1 and Table 1, it is observed that for the oxide silicon sample was an intense signal in silica X-ray fluorescence, with a weight percent of the sample of 96.77 % silica and barely 1.62% alumina.

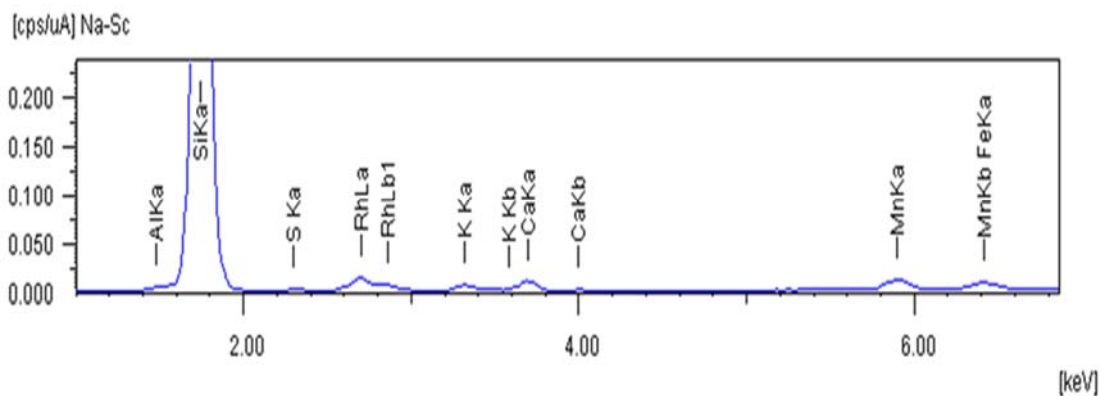


Figure 1: X-ray fluorescence (Na-Sc) silica extracted from rice husk

Table 1: Results of quantitative X-ray fluorescence silica extracted from rice husk

Name	Analyte (oxide)	Result (%)	Standard Deviation
Silicon	SiO ₂	96.77	0.120
Aluminum	Al ₂ O ₃	1.62	0.041
Calcium	CaO	0.60	0.007
Potassium	K ₂ O	0.47	0.007
Manganese	MnO	0.26	0.003
Iron	Fe ₂ O ₃	0.16	0.002
Sulfur	SO ₃	0.10	0.007
Zinc	ZnO	0.02	0.001
Copper	CuO	0.01	0.001
Lead	PbO	0.01	0.001

Quantification of phases present in calcium phosphates evidenced that the material had a total of 88.9 % crystalline and 11.1 % amorphous, 38.1 % tricalcium phosphate, 15.7 % hydroxyapatite and calcium phosphate (Ca₂P₂O₇) 35.1 %. The synthetic biocomposite therefore has a structure with crystalline and amorphous phases.

SEM-EDS were performed to the material after degradation. Figure 2 shows an elemental analysis by energy dispersive spectroscopy X-ray (EDS) for 30-70 % w / w calcium phosphate and silicon oxide showing an atomic composition of 54.96 %, 28.83 %, 9.79 %, 3.24 %, 1.14 % and 0.55 % for the elements silicon, oxygen, calcium, phosphorus, magnesium and aluminum respectively, keeping the silica surface at a higher rate, in the presence of calcium and phosphorus, which shows compositional stability of the material. The coating after the electrochemical tests, is quite porous and with different grain sizes.

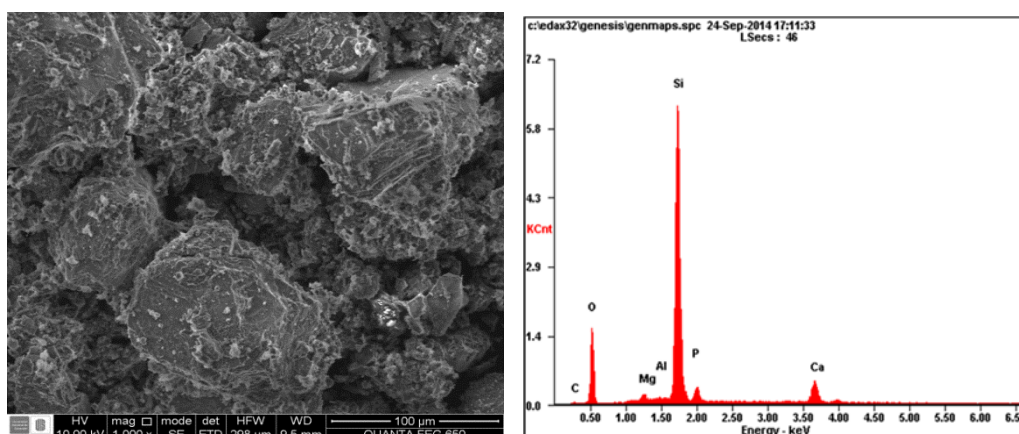


Figure 2. SEM-EDS for composite 30-70% w / w calcium phosphate-silica, respectively.

3.2 Electrochemical characterization

Values more noble corrosion potential, belong to the coatings, being the noblest coating 70-30 % w / w calcium phosphate-silicon oxide (see Figure 3). The noblest potential indicate that at the beginning of the electrochemical tests, the coatings are stable, but more than Ti6Al4V. This agrees with the results found in the degradation test for 7 days (Montañez and Peña, 2015).

The technique of electrochemical impedance spectroscopy shows two diagrams, one is the Bode plot, where is the change in frequency impedance module. The other graph is the Nyquist diagram, where the capacitive and resistive impedance component, or what is the same, the imaginary impedance and the actual impedance Zimag and Zreal respectively. In the Bode and Nyquist diagrams can be detected both charge transfer and mass. Figure 4 shows the Bode plot for biocomposites 70-30 and 30-70 % w / w calcium phosphate and silicon oxide, respectively, as well as for Ti6Al4V. For all three cases, there are two time constants, showing the layers formed, that for the coatings are of different concentrations of calcium phosphate and silicon oxide, while for the reference sample Ti6Al4V is the oxide formed in the process corrosion of the sample. The values

of impedance module of the coatings are less than the reference sample, indicating the susceptibility of the coatings to degradation.

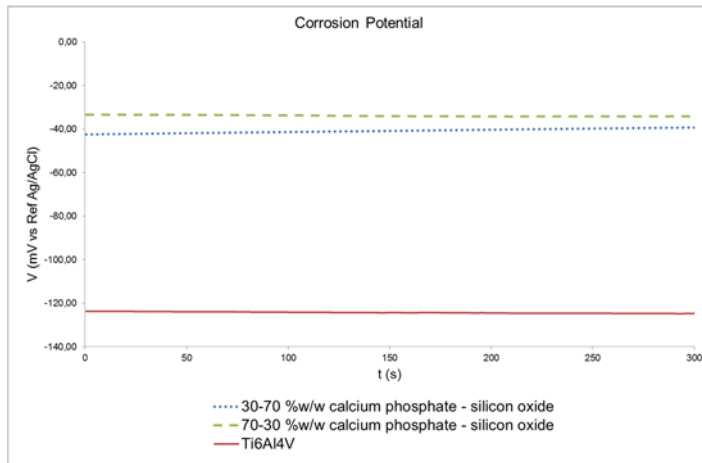


Figure 3: Corrosion Potential

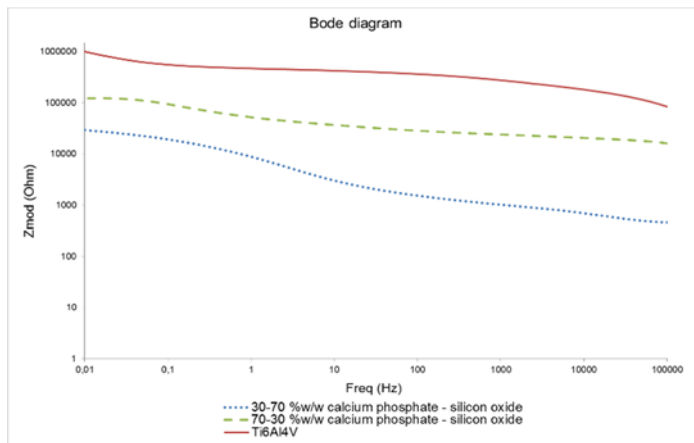


Figure 4. Electrochemical impedance spectroscopy: Bode plot

In the Nyquist plot (Figure 5), again they show two time constants, one at low frequencies, indicating the charge transfer between the surface and the electrolyte, and another at high frequencies with mass transfer, that for coatings they have low impedance values with respect to the reference sample, and can be explained by the decrease of the concentration of a species on the surface, involved in the mechanism of dissolution of the coating, whereas for the Ti6Al4V indicates the formation of a oxide on the surface of the material passively therein.

The diagrams of polarization resistance show the resistance value for each test. Using standards as: ASTM G-102 (ASTM, 2010) and ASTM G-59 (ASTM, 2014) and applying the technique of polarization resistance, the corrosion current and the rate of degradation of the coatings was estimated by the Stern-Geary equation (Durgalakshmi et al., 2015). In Figure 6, a fairly steep slope for the reference sample with a value of 1.119×10^9 , which is already known as evidenced, this titanium alloy has a good corrosion resistance, while the values of the coatings are 1.049×10^8 and 3.052×10^7 are lower, indicating the dissolution of the porous coating, however, these corresponding to the polarization resistance values are not lower with respect to other materials.

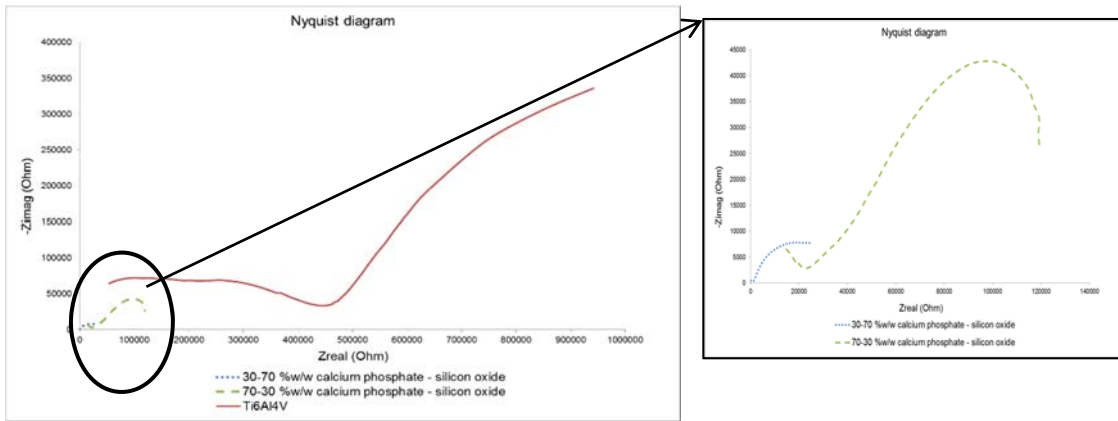


Figure 5. Electrochemical impedance spectroscopy: Nyquist plot

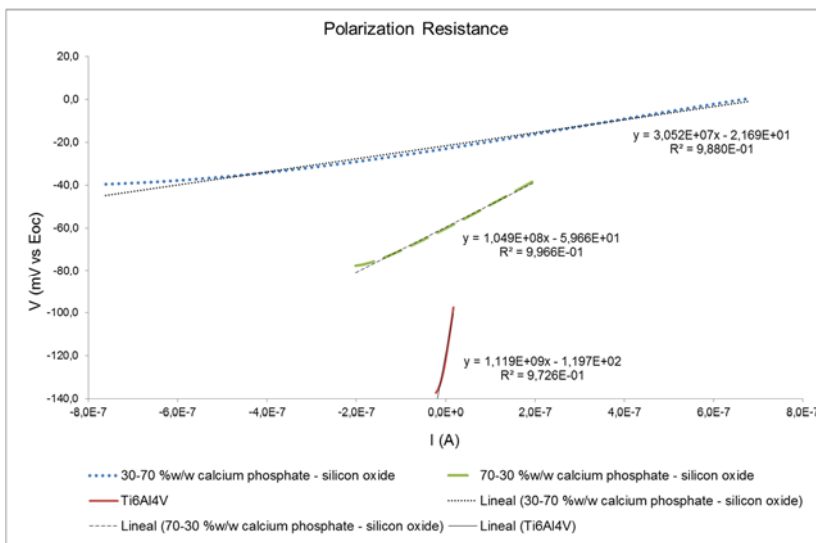


Figure 6. Polarization resistance test.

The degradation rate values, found from the corrosion current (I_{corr}) are calculated. The values presented degradation rate was 0.00389 mm / year; 0.00166 mm / year and 0.00010 mm / year to 30-70 % w / w calcium phosphate - silicon oxide; 70-30 % w / w calcium phosphate - silicon oxide and Ti6Al4V respectively.

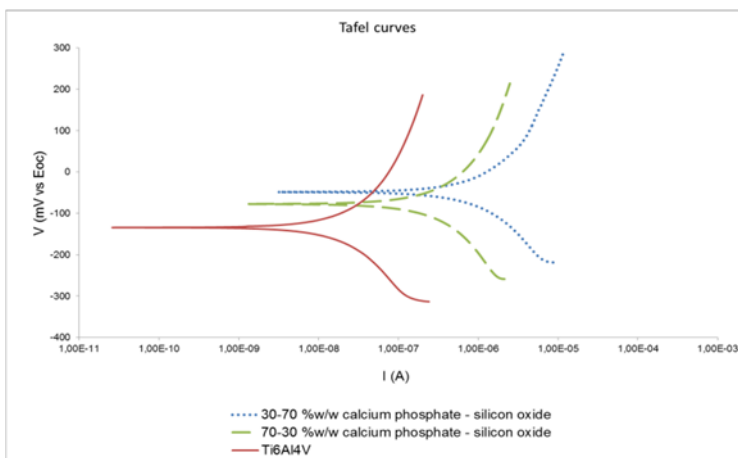


Figure 7. Tafel curves

It is evident that the coatings have a high degradation rate with respect to the reference sample, mainly due to the decrease in the concentration of calcium and phosphorus in the coated due to dissolution of the coating surface, the corrosion resistance decreases because the coatings are porous, and the breakdown potential decreases (Durgalakshmi et al., 2015).

In Figure 7, the Tafel curves for the two coatings and the reference sample shown. The curve shift to the right, indicating that the coating is degraded with the time, however, the upward shift indicates that the surface is more stable, consistent with the results found in corrosion potential, this surface being less susceptible to corrosion of the alloy Ti6Al4V.

4. Conclusion

Calcium phosphate coatings - silicon oxide show degradation on the surface of the base material, according to degradation rates calculated from the corrosion current. The coating with the best performance in terms of coating degradation is 70-30% w / w calcium phosphate - silicon oxide. The surfaces become more stable when Ti6Al4V alloy is coated with the synthetic biocomposite, evidenced by diagrams corrosion potential and Tafel curves. After the electrochemical degradation, the coating contains the main elements calcium, phosphorus and silicon, which ensures the stability of the compositional while feature that makes it attractive for biomedical, especially the application of bone filler degrades field.

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