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Improving the bond strength of bioactive glass coatings obtained by atmospheric plasma spraying

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ABSTRACT

Bioactive glasses are inorganic biomaterials that can provide a bioactive response and thus favor the successful bonding of orthopedic implants. Some strategies were studied to improve the bond strength of bioactive glasses, such as producing agglomerated bioactive glass powders or designing different coatings combining hydroxyapatite (HA) with bioactive glass. The bioactive coatings were produced by atmospheric plasma spray (APS) onto titanium alloy substrates, and the microstructure and adhesion strength of the developed coatings were evaluated. It was found that a significant improvement in adhesion strength was obtained for the developed coatings, in particular when thermal treatment was applied to pure glass coatings and when HA was part of the coating. The coatings reactivity in simulated body fluid and Tris-HCl solutions was studied. All coatings showed bioactive behavior, but the ones with only an amorphous phase in the upper part of the coating dissolved faster, releasing a larger proportion of Ca ions, which caused faster nucleation and growth of apatite deposits.

1. Introduction

Implant modification by developing coatings on its surface is considered one of the most effective techniques to promote the osseointegration of implanted biomaterials [1]. In order to achieve good implant anchorage, it is essential that the coating remains well adhered to the substrate until a good bond with the bone tissue is obtained [2]. Nowadays, thermal spraying, particularly atmospheric plasma spraying (APS), is one of the most common methods to produce bioactive ceramic coatings [3].

APS is a deposition technique where the powder is injected in the plasma by a carrier gas, usually argon. The powder particles are melted and accelerated to the substrate forming the coating during the process. The mixture of argon and hydrogen was modulated to produce the proper plasma jet that enables the melting and acceleration of the particles. This adjustment depends on the characteristics of the feedstock powder [4]. The high temperatures of the plasma allow the deposition of powder materials with high melting temperatures and low thermal conductivity, such as ceramics [3,5,6].

Increasing the lifetime of implants and their success rate is one of the significant challenges in orthopedic implant technology. Hydroxyapatite (HA) coatings produced by APS have been widely used and accepted in medicine in the last decades [3,7]. However, the failure rate of

implants, either due to insufficient osseointegration or infection, leaves room for improvement [8–11]. Developing new bioactive coatings is an interesting approach to addressing that issue.

Bioactive glasses are a family of glasses with unique properties due to a more open structure than conventional glasses [12]. Bioactive glasses were discovered in 1969 by L.L. Hench [13] and arrived at the medicine as a promising material capable of bonding to hard and soft tissues. Furthermore, these reactive glasses exhibit an encouraging cellular response compared to other biomaterials [14].

Bioactive glass coatings have been developed using techniques such as electrophoretic deposition, sol-gel, enameling, laser cladding, or thermal spraying. However, the large difference in coefficient of thermal expansion (CTE) between the metallic biomaterials and the bioactive glass coatings makes obtaining enough coating adhesion to commercialize them challenging. In order to use these coating materials, an improvement in their adhesion strength becomes necessary. Minimum bond strength of 22 MPa can ensure the mechanical integrity of the coatings according to international regulations. In a previous study [15], the authors applied heat treatment to a bioactive coating to improve the bonding with the metallic substrate. The coating obtained doubled the adhesion value with the heat treatment, reaching a bond strength of 17 MPa. Moreover, other authors reported bond strength values of pure bioactive glass coatings deposited by various thermal spray technologies

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below 10 MPa [16,17].

The present work aims to deeply evaluate strategies to overcome the low adhesion of bioactive glass coatings deposited by APS. During the present investigation, different approaches were considered: changing the morphology of the feedstock powders since this new arrangement of the material could favor the adhesion with the substrate; incorporating HA as support material, taking advantage of the good adhesion of HA with the metallic substrate, and applying heat before or after the spraying process to reduce internal stresses in the coating that could affect the bond to the substrate. The developed coatings were studied, analyzing, in particular, their mechanical and biological properties. The objective was to create a coating with suitable mechanical properties while ensuring its bioactivity.

2. Experimental methods

2.1. Powder and substrate

Two commercial powders were used to produce the designed coatings: a sintered HA Capital®30 powder (Plasma Biotol Limited, United Kingdom) with crystallinity above 95 % and a bioactive glass powder 45S5 (Denfotex Research, United Kingdom) manufactured by the usual melt-quenching method. The same bioactive glass powder was used to produce the agglomerated powders.

Titanium G5 (Ibermetal, Spain) was used as substrate material. Particularly, discs with 25 mm diameter and 10 mm height were used for tensile strength tests. Rectangular substrates measuring $100 \times 20 \times 5$ mm were used for the metallographic characterization of the coatings. Finally, for the in vitro studies, coatings were deposited onto discs with a diameter of 9 mm and thickness of 1 mm.

2.2. Agglomeration of powder

The agglomeration of bioactive glass powders was performed in a conventional method, where a binder was used to join the powder particles, which later was removed by heating [18].

Firstly, the 45S5 commercial powder was milled using planetary ball mill equipment (PM 400, Retsch, Haan, Germany), with Y-ZrO₂ balls of 5 and 10 mm diameter and grinding jars of the same material. The revolution speed was fixed at 400 rpm, and grinding was done for two hours since no further particle size reduction was observed for longer processes. The size reduction of the particles was produced by the friction and the high impact that particles suffered during the process.

Once the powder was milled, a sieving step was done to remove the large particles. The collected fraction below 40 µm was combined with a polyvinyl alcohol (PVA) solution (10 g of PVA 87–90 % hydrolyzed in 150 mL of Milli-Q water) until a semi-wet state of the powder was reached. The amount of PVA solution added to the milled powders was adjusted to achieve proper agglomerates; the best results were observed when adding 0.2 mL of solution per gram of milled powder.

After incorporating the binding agent, powders were spread on an aluminum foil and dried at room temperature for 24 h. Subsequently, a sieving step was done to collect a fraction between 20 and 80 µm, a proper size for APS [19,20].

The final step consisted in removing the binder agent. For this purpose, agglomerated particles were heated using a high-temperature chamber furnace (CRN 4–18, Hobersal, Barcelona, Spain). The heating rate was 10 °C/min up to 500 °C, followed by a dwell step of 1 h and finally cooling to room temperature at 10 °C/min. The burnout of the binder was done at 500 °C, above the degradation temperature of the PVA, which occurs between 200 °C and 300 °C [18], and below the glass transition temperature of the bioactive glass (550 °C) to avoid any phase transformation [21].

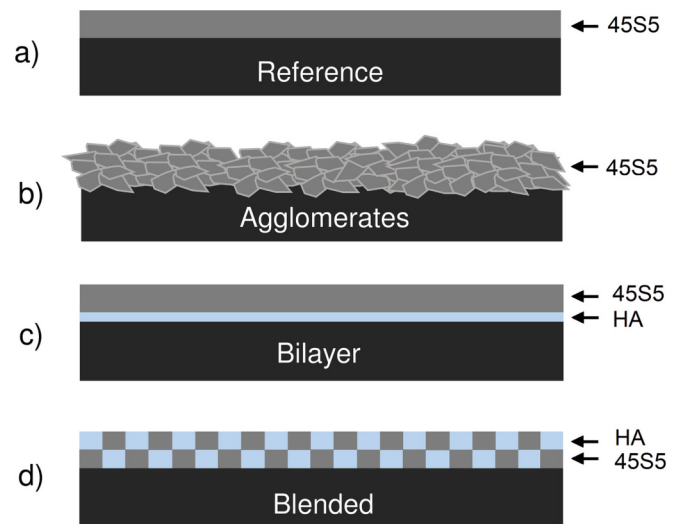


Fig. 1. Designed coatings: a) reference, b) agglomerates, c) bilayer, and d) blended.

Table 1

References of the different coatings developed.

Reference name	Pre-treatment	Post-treatment
Reference	–	–
Reference SH	Surface heating	–
Reference TT	–	Thermal treatment
Agglomerates	–	–
Agglomerates SH	Surface heating	–
Agglomerates TT	–	Thermal treatment
Bilayer	–	–
Bilayer SH	Surface heating	–
Bilayer TT	–	Thermal treatment
Blended	–	–
Blended SH	Surface heating	–
Blended TT	–	Thermal treatment

2.3. Design of coatings

The different strategies addressed to enhance the bond strength of the bioactive glass coatings are represented in Fig. 1. The first coating designed involved agglomerated 45S5 particles, produced as described previously (agglomeration of powder). This coating was named “agglomerates”. The second coating consisted of an anchor layer of HA between the glass and the titanium alloy to mitigate the significant difference in CTE between these materials. This coating was called “bilayer”. Another coating comprised a manual blend of HA and 45S5 powders in a 1:1 ratio by weight. This coating was named “blended”. Finally, a coating produced with the bioactive glass powder was used for comparison purposes, this coating was called “reference”.

Furthermore, two different approaches were considered for the developed coatings to reduce the residual stress and enhance the coating adhesion of the bioactive glasses with the substrate. First, the effect of pre-heating the substrate immediately prior to deposition was assessed. The heating was applied by scanning the torch over the surface of the substrate for one complete cycle and maintaining the same spraying conditions. The pre-heating temperature (218 ± 2 °C) was measured with a thermometer thermocouple (PCE-T390, PCE Instruments, Durham, United Kingdom). The second approach consisted of applying a post-thermal treatment at 725 °C for 5 h to the coatings, following the process described in our previous research [15]. The twelve coatings performed are listed in Table 1, indicating if a pre or post-treatment was applied.

Table 2

Plasma spraying parameters used to produce the coatings.

	Type A	Type B
Primary gas (Ar), flow rate (slpm)	35	50
Secondary gas (H ₂), flow rate (slpm)	12	1
Arc Current (A)	600	500
Stand-off distance (mm)	80	80

2.4. Coating deposition

For the coating deposition, APS equipment (Plasma-Technik A3000S, Sulzer Metco AG, Wohlen, Switzerland) with an F4 plasma

torch was used, with argon as the primary carrier gas and hydrogen as the secondary gas for the plume formation. The powders were deposited onto titanium alloy substrates previously grit blasted (MAB-4, MAB industrial, Barcelona, Spain) with corundum G24 (grit size 800 μm) at a pressure of 0.5 MPa. Before the spraying process, the substrates were cleaned with ethanol.

The parameters used for coating deposition were selected according to the powder characteristics. For the glass powder, the chosen parameters provided quite energetic conditions to achieve the melting of the glass powder; these parameters are referred to as type A in Table 2. The parameters selected for the HA powder were determined by the results found in a previous study [22] that analyzed the influence of some

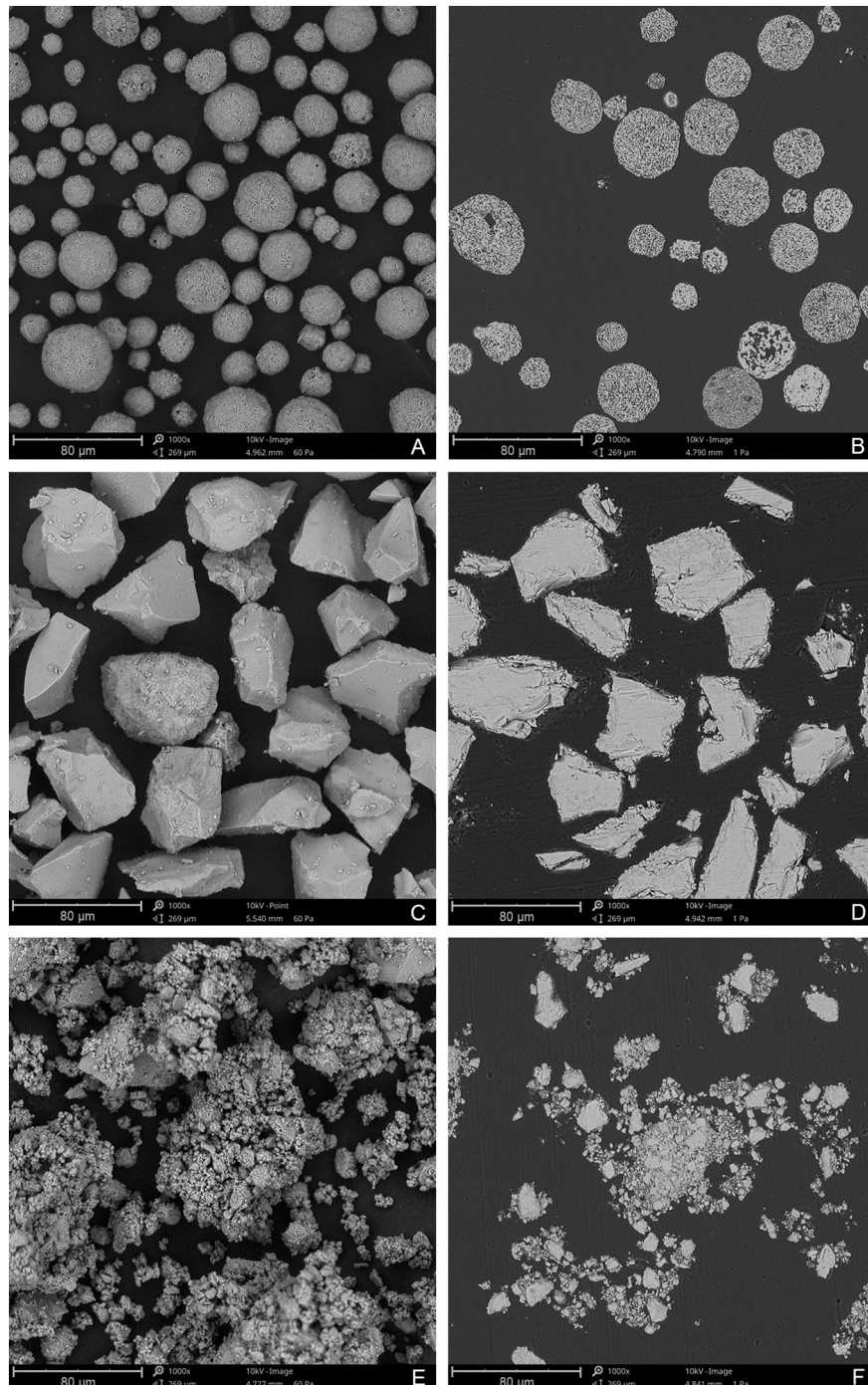


Fig. 2. Free surface and cross-section of powders: (A,B) HA, (C,D), 45S5 bioactive glass, and (E,F) 45S5 agglomerated.

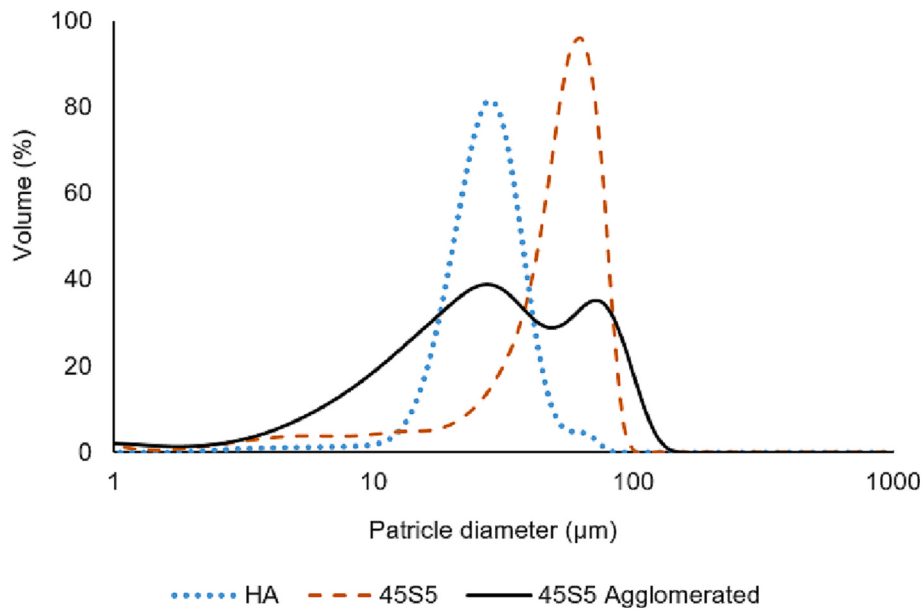


Fig. 3. Particle size distribution in volume of the powders.

spraying parameters on different properties, such as crystallinity, adhesion strength, and thickness. These parameters are determined as type B in Table 2.

The reference and agglomerates coatings and the top layer of bilayer coating were produced using type A spraying conditions. The blended coating was sprayed using type B conditions because the high plasma energy involved in type A caused severe phase changes in HA, and the quality of that coating was unsatisfactory. Then, the blended coating and the lower layer of the bilayer coating were deposited using type B conditions.

2.5. Characterization of the powder and coating

The morphology and microstructure of the powders and coatings were determined using a scanning electron microscope (SEM) (Phenom ProX, Phenom-World BV, Eindhoven, The Netherlands) equipped with energy-dispersive X-ray diffraction. The samples were prepared by cold mounting resin, abraded with silicon carbide abrasive papers up to P4000 (grit size 5 μm), and polished with 1 μm diamond slurry to analyze the cross-sections of powders and coatings. Before the microscopy studies, the samples were coated with a gold layer to make them conductive using an SEM coating unit (E-5000, Polaron, Watford, England).

Each powder was tapped regularly in a graduated cylinder to settle the powder inside the cylinder. The filling and tapping process was repeated until the volume of the powder remained fixed at 5 mL. When this occurred, the amount of powder used was weighted. This way, the tapped density of the different powders was measured.

The particle size distribution of the sieved powders was determined using a laser diffraction particle size analyzer (LS 13 320, Beckman Coulter, California, USA).

A mechanical testing machine (ME-402/10, Servosis, Madrid, Spain) was used following the ASTM C633-13 (Standard test method for adhesion or cohesion strength of thermal spray coatings) to determine the bond strength of the coatings. Three coated samples of each type were glued to grit-blasted counter-test pieces using HTK ULTRA BOND 100® glue (HTK, Germany). Then, perpendicular tensile stress was applied to the coating with the displacement rate set at 0.02 mm/s until fracture occurred. In addition to performing the test on the developed coatings, it was also done after one day of immersion in hank's balanced salt solution (HBSS) (Sigma-Aldrich, Germany) at 37 °C.

The crystallographic structure of the coatings before and after the thermal treatment was analyzed by X-ray diffraction (XRD) using a diffractometer (X'Pert PRO MPD, PANalytical, Cambridge, UK).

2.6. Ability to form apatite and degradation assessment

The bone-bonding ability of the coatings was evaluated by an in vitro test following ISO 23317 (Implants for surgery - In vitro evaluation for the apatite-forming ability of implant materials). The HCA formation was evaluated at different periods (0, 3, 7, and 14 days). Three samples of each coating type were immersed, in a vertical position, in HBSS solution inside polypropylene containers placed in a thermostatic bath with agitation at 37 °C. The solution was refreshed twice a week to avoid ionic saturation. After each period, samples were rinsed with ultra-pure water and dried for 24 h at room temperature.

The surface inspection of the samples using the SEM equipment assessed the formation of the HCA layer on the coatings at different periods. Before this observation, all the samples were coated with a gold layer to increase their conductivity. Furthermore, the cross-section of the formed layer was analyzed for the samples immersed during the most prolonged period. For this examination, the cross-sections were prepared as described previously.

The degradation behavior of the different bioactive coatings was evaluated following the specifications of ISO 10993-14 (Biological evaluation of medical devices - Part 14: Identification and quantification of degradation products from ceramics). Samples were immersed in a buffered solution consisting of Tris-HCl with pH adjusted to 7.4 ± 0.1 at 37 ± 1 °C for 120 h. After the test, the samples were rinsed with ultra-pure water and dried overnight at 120 °C. The loss of weight suffered by the samples was determined by measuring their weight before and after the test with a high-precision scale (CPA225D, Sartorius, Göttingen, Germany). Moreover, pH variation caused by the dissolution process was analyzed by recording the pH values after the test using a universal pH meter (Hach, Spain). The concentration of elements released from the coatings (silicon, calcium, phosphorus, and sodium) was determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8300, PerkinElmer, Waltham, USA).

Table 3

Tapped density and particle size distribution in volume of the powders.

	Tapped density (g/cm ³)	d ₁₀ (μm)	d ₅₀ (μm)	d ₉₀ (μm)
HA	1.4	18	29	42
45S5	1.4	11	55	78
45S5 Agglomerated	0.9	7	29	83

Table 4

Bond strength of the designed coatings before and after one day of immersion.

Coating type	Bond strength (MPa)		Bond strength loss after one day of immersion (%)
	Without immersion	After one day of immersion	
Reference	8 ± 3	4 ± 1	43
Reference SH	11 ± 1	4 ± 1	68
Reference TT	17 ± 1	6 ± 1	67
Agglomerates	13 ± 2	6 ± 1	52
Agglomerates SH	16 ± 3	10 ± 1	37
Agglomerates TT	25 ± 3	10 ± 1	63
Bilayer	19 ± 2	3 ± 1	83
Bilayer SH	24 ± 2	9 ± 3	63
Bilayer TT	22 ± 3	5 ± 2	78
Blended	22 ± 4	13 ± 3	41
Blended SH	20 ± 1	13 ± 1	35
Blended TT	24 ± 2	8 ± 2	68
HA	≈ 39 ± 5	≈ 8 ± 3	81

3. Results and discussion

3.1. Powder characterization

The SEM analysis performed on the powders allowed us to establish their morphology and size differences, as seen in Fig. 2. Notably, the particles of HA powders show a spherical morphology composed of small particles forming aggregates. This microstructure is typical for agglomerated and sintered powder, where small particles are compacted and bonded by applying heat and pressure. The cross-section of the HA powders also reveals some porosity. On the contrary, the 45S5 glass particles are dense and irregular, with corners and sharp edges. This shape is consistent with the manufacturing process where the material is crushed after the melt-quenching. Moreover, the particles observed are similar in size to each other. Finally, the agglomerated powders are composed of small particles of approximately 1 to 20 μm. These

aggregated particles present an irregular and porous morphology.

The particle size distribution of the powders measured by laser diffraction can be observed in Fig. 3, and the characteristic values related to their size distribution are found in Table 3. HA powder, represented by a dotted line, exhibits a narrow distribution; most particles are from 20 to 40 μm. For glass particles, the distribution is also in a narrow range, represented by a dashed line, but in that case, most of the particles have a size between 10 and 80 μm. By contrast, the manufacturing process of the agglomerated powder has resulted in a broader particle size distribution with a bimodal nature, represented by the solid line in the graph. The values obtained with this technique are consistent with the observations by microscopy.

The values of the tapped density are shown in Table 3. It can be seen how the change in morphology of the glass particles caused a notable reduction in the density of the agglomerated powders when compared to the original glass powder.

3.2. Bond strength tests

When the osseointegration process starts, the interface must remain immobile for the bond to form. For this purpose, the coating should stay well adhered to when the device is implanted and thus facilitate a good bonding with the bone tissue. During the osseointegration process, the stability of the implant-bone fixation depends on the initial mechanical stability that decreases over time while biological stability increases. It is crucial to notice that when osseointegration is accomplished, the strength of the bioactive bond formed is equal to or stronger than that of the host bone [23].

In the first part of the study, the bond of the coatings listed in Table 1 and, additionally, pure HA coatings were evaluated. The bond strength results of the coatings without immersion and after one day of immersion in physiological solution are detailed in Table 4, Fig. 4, and Fig. 5. For a better evaluation of the results, the minimum value required for non-immersed coatings according to regulations and the mean value of pure HA coating after one day of immersion were represented in these figures. In addition, Fig. 6 and Fig. 7 show the details of the fracture morphologies of some of the coatings tested.

The first design to improve the bonding of the coating with the substrate consisted of modifying the morphology of the feedstock powder. Through agglomeration, a powder with lower density, higher porosity, and higher specific surfaces was obtained compared to the commercial glass powder. A notable increase in bond strength was observed when comparing agglomerates coatings to the reference coatings for the same spraying conditions (13 ± 2 MPa concerning 8 ±

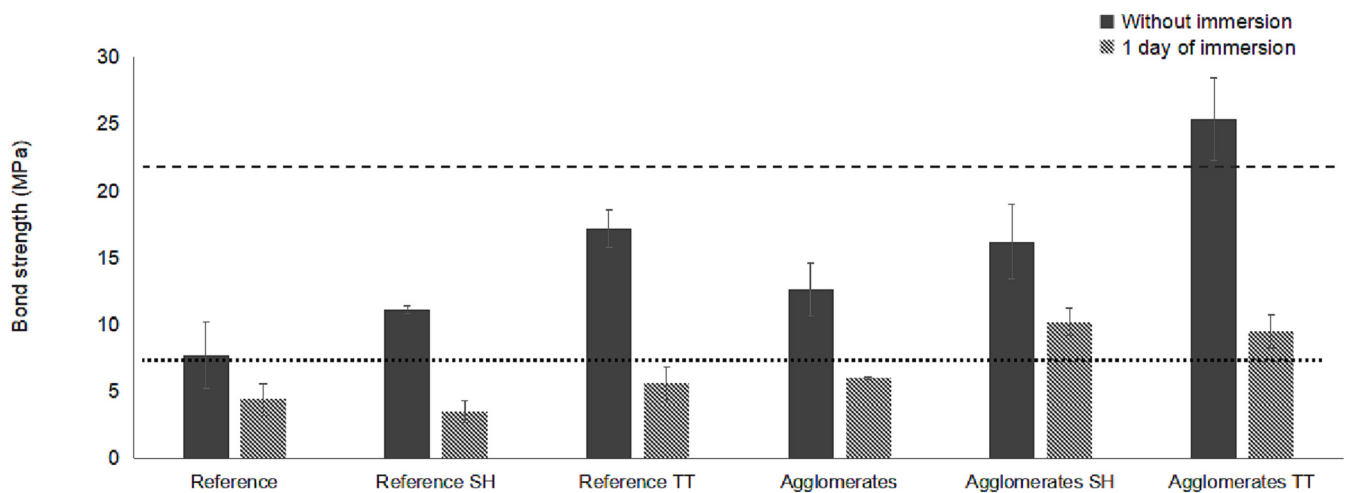


Fig. 4. Bond strength of the bioactive glass pure coatings without immersion and after one day of immersion in HBSS solution (slashed line: minimum value required for non-immersed coatings according to regulations; dotted line: the mean value of pure HA coating after one day of immersion).

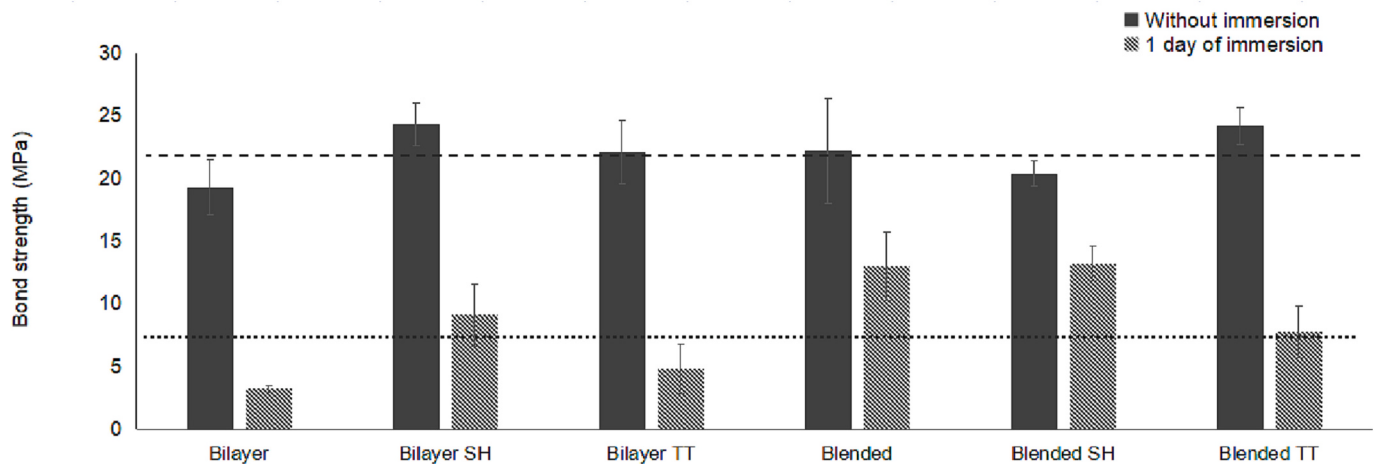


Fig. 5. Bond strength of the coatings incorporating HA without immersion and after one day of immersion in HBSS solution (slashed line: minimum value required for non-immersed coatings according to regulations; dotted line: the mean value of pure HA coating after one day of immersion).

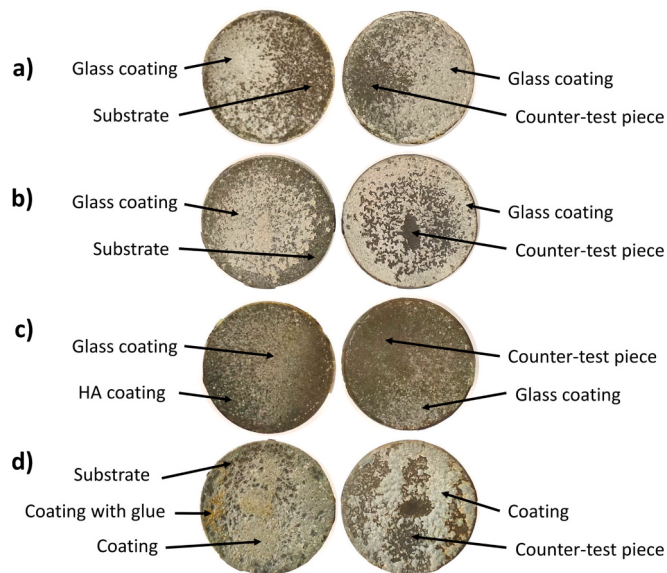


Fig. 6. Fracture morphology of coatings: a) reference, b) agglomerates, c) bilayer, and d) blended. Samples on the left correspond to coated samples, and on the right to counter-test pieces.

3 MPa). The fracture occurred mainly through the glass coating in both cases, as shown in Fig. 6-a) and -b). The results may suggest that agglomerated powders melt more quickly than commercial particles as the agglomerated powder has high porosity and is composed of smaller particles that cause faster material heating [24]. Thus, the proper melting of the particles can favor the bond with the substrate and therefore increase the bond strength.

Another of the strategies developed to improve the bonding of bioactive glass coatings involved the incorporation of HA. HA has a high acceptance and commercialization in the orthopedic and dental implant field; however, it has a lower bioactive capacity than bioactive glasses. In this line, two types of coatings were considered: bilayer, which included an intermediate layer of HA between the substrate and the glass layer, and blended, formed by the mixture of HA and glass powders. In both cases, HA caused a significant improvement (more than twice) in the bond strength of the coatings compared to the reference coating. The primary mechanism related to the residual stresses, which affect the integrity of the coatings, occurs after deposition, during the cooling process to room temperature. A significant mismatch of the CTEs of different materials is why large residual stresses resulted after cooling [25]. The enhancement of the bond strength with these strategies can be explained by the minor mismatch of the CTE between the HA ($13.9 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [26]) and the $\text{Ti}_6\text{Al}_4\text{V}$ ($9.5\text{--}10.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [27]) than that between the 45S5 ($15.1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [28]) and the substrate. Moreover, the failure of the bilayer coatings occurred mainly between the HA and bioactive glass layer as shown in Fig. 6-c. In the case of blended coatings,

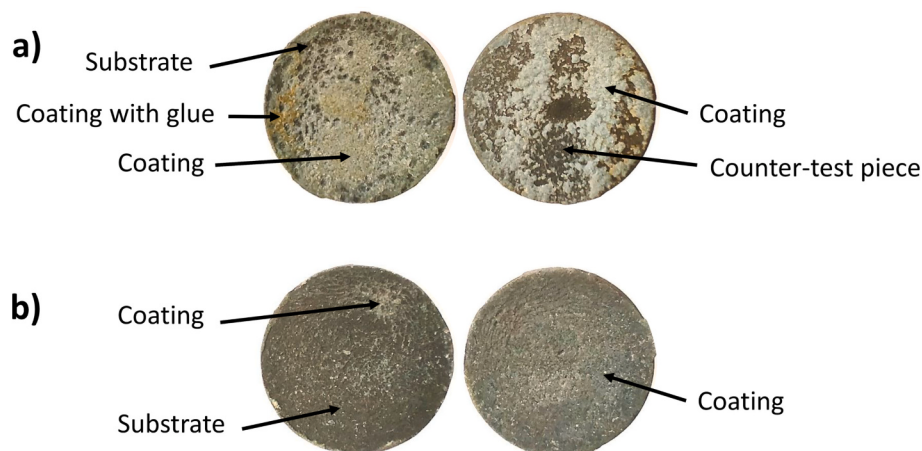


Fig. 7. Fracture morphology of coatings: a) blended, and b) blended SH. Samples on the left correspond to coated samples, and on the right to counter-test pieces.

Table 5

Percentage of bond strength increase with pre and post-treatments compared to the same coating type (SH: surface heating and TT: thermal treatment).

Coating type	Bond strength increase coating type (%)	
	SH	TT
Reference	44	123
Agglomerates	29	102
Bilayer	26	15
Blended	-8	9

the failure happened through the coating, as observed in Fig. 6-d. However, it occurred through specific coating areas, revealing parts of the coating with different adhesion because of the arbitrary distribution of the deposited materials.

In general, the influence of surface heating resulted in a substantial increase in bond strength, as seen in Table 5. Pre-heating the substrate does not affect its roughness, the values recorded for pre-heated substrates ($R_a = 6 \pm 1 \mu\text{m}$ and $R_z = 36 \pm 3 \mu\text{m}$) are almost equal than after grit blasting process ($R_a = 6 \pm 1 \mu\text{m}$ and $R_z = 38 \pm 3 \mu\text{m}$). Changes in the microstructure or surface chemistry of the pre-heated substrates concerning the grit-blasted ones are not observed. The stress generated at the interface can explain the bond strength increase. The significant temperature difference between the impinging particles onto the unheated substrate gives rise to high interface tensions [29]. Thus, by pre-heating the substrate, the mitigation of the rapid cooling of glass droplets in the first layer is achieved and reduces the stress generated in the deposited particles. In particular, for the blended coating, this pre-heating of the surface did not cause an enhancement in adhesion, and the failure turned to adhesive, as occurred in the interface with the substrate (Fig. 7). Applying the pre-heating did not affect the bond failure mode for the other studied coatings.

Applying the thermal treatment resulted in greater adherence to the coatings and did not affect the failure mode of the studied coatings respect to the coating without post-treatment. This increase was exceptionally high for coatings containing only bioactive glass, increasing adhesion by 123 % for the reference coatings and 102 % for the agglomerates. The enhancement of mechanical properties of glass materials by a thermal treatment has been demonstrated in previous studies [15,30,31]. When heating is done above the glass transition temperature of the glass, a viscous state is achieved that allows better inter-particle cohesion and stress relaxation. Moreover, the crystallization of some phases formed during the post-treatment improves the material's mechanical properties. In particular, in Fig. 8, it can be seen that the crystalline phase $\text{Na}_6\text{Ca}_3\text{Si}_6\text{O}_{18}$ (Ref. code: 01-079-1089) was generated for both the reference TT and the agglomerates TT after the thermal treatment.

In line with the regulations (ASTM F1147-05 Standard Test Method for Tension Testing of Calcium Phosphate and Metallic Coatings), calcium phosphate and metallic coatings adhered to dense metal substrates require a minimum adhesion strength of 22 MPa to be suitable for orthopedic applications. The coatings that meet this requirement are agglomerates TT, bilayer SH, bilayer TT, blended, and blended TT.

It is essential that when the coatings are in contact with physiological fluid, as occurs when they are implanted, the impact on bond strength is moderate since a good fixation promotes the stability and success of the implants. The different coatings' adherence was also analyzed after one day of immersion in the physiological solution for further assessment. The bond strength value corresponding to pure HA coating is 39 ± 5 MPa and after one day of immersion, the HA coating suffered a severe loss of bond strength (7 ± 3 MPa), as seen in Table 4.

Moreover, it should be noted that agglomerates SH, agglomerates TT, bilayer SH, blended, blended SH, and blended TT coatings have a greater bond strength after one day of immersion than HA coating.

The bond strength study showed that a change in the morphology of the original glass particles could improve the bond with the substrate.

Furthermore, incorporating HA as a bond coat and blending with the feedstock powder helped achieve better-adhered coatings. Pre-heating the substrate increased the bond strength of the pure glass coatings, around 30 to 45 %, when compared to the original type of coating. While applying a post-thermal treatment at 725 °C caused a more significant increase for pure glass coatings, between 100 and 125 % compared to the original ones. The analysis of the bond strength of the coatings after one day of immersion in a physiological solution revealed a pronounced decrease in that property compared to the coatings without immersion. In general, the loss of adherence for the designed coatings is lower than for the HA coatings. Regarding the bond strength requirements for coating implants, agglomerates TT, bilayer SH, and blended coatings presented the more interesting results for samples with and without immersion in physiological solution.

3.3. *In vitro* bioactivity study - ability to form apatite

In addition to having a good bond strength, the coatings must also have the ability to stimulate bone regeneration. When bioactive glasses are in contact with fluids simulating the ionic composition of the body fluids, the reactivity of the bioactive glasses leads to a cascade of surface reactions that starts from the release of ions belonging to the glass structure and ends with the formation of a bone-like apatite layer on its surface. Therefore, bioactivity and degradation tests were performed to evaluate the biological response of the coatings in physiological solution. This part of the study was conducted on some of the developed coatings. Since this part of the study mainly affects the upper part of the coating, SH coatings were dismissed due to their similarity with their analogs. Only the agglomerates TT was selected for the thermally treated samples since the adhesion improvement for the coatings containing HA was very slight, and the reference TT was already analyzed in our previous study [15]. Thus, the coatings considered for this part of the study were: reference, agglomerates, agglomerates TT, bilayer, and blended.

The biomaterials forming the coatings, bioactive glass and HA, are expected to provide bioactive capacity to the samples. Due to the importance of the HCA layer formation in the osseointegration process, the coatings were immersed in a physiological solution for fourteen days. The surface of the coatings was periodically evaluated to analyze the kinetics of forming an HCA layer on their surfaces.

Fig. 9 shows the surface of the coatings before the test and after three and fourteen days of immersion in HBSS. SEM images of the samples without immersion allow us to know the surface before beginning the process of formation of the apatite layer. The surfaces of the coatings formed by agglomerated particles (agglomerates and agglomerates TT) showed high porosity, particularly coatings that were not heat treated since heating can reduce the porosity [32]. Fingered splats corresponding to molten glass particles were observed on the surface of reference and bilayer coatings. While on the surface of the blended coatings, it is possible to appreciate the presence of HA particles in combination with glass particles.

The formation of the HCA layer begins with the nucleation of small apatite spheres, which grow, and form aggregated deposits. The continuous formation and growth of apatite deposits lead to a layer covering the bioactive material. After three days of immersion, reference, agglomerates, and bilayer coatings showed a continuous layer of HCA on their surface, revealing the rapid growth of the apatite layer on these surfaces. On the surface of the blended and agglomerates TT coatings, it is possible to appreciate the presence of small spheres of apatite since these coatings are still in an early stage of the HCA layer formation. In addition, it can be seen how in the blended coating, apatite deposits were formed on top of glass particles, which are more reactive than HA areas. In the final period, the surface of all the coatings was fully covered by a continuous HCA layer.

The test results suggest that reference, agglomerates, and bilayer coatings promote fast HCA layer growth.

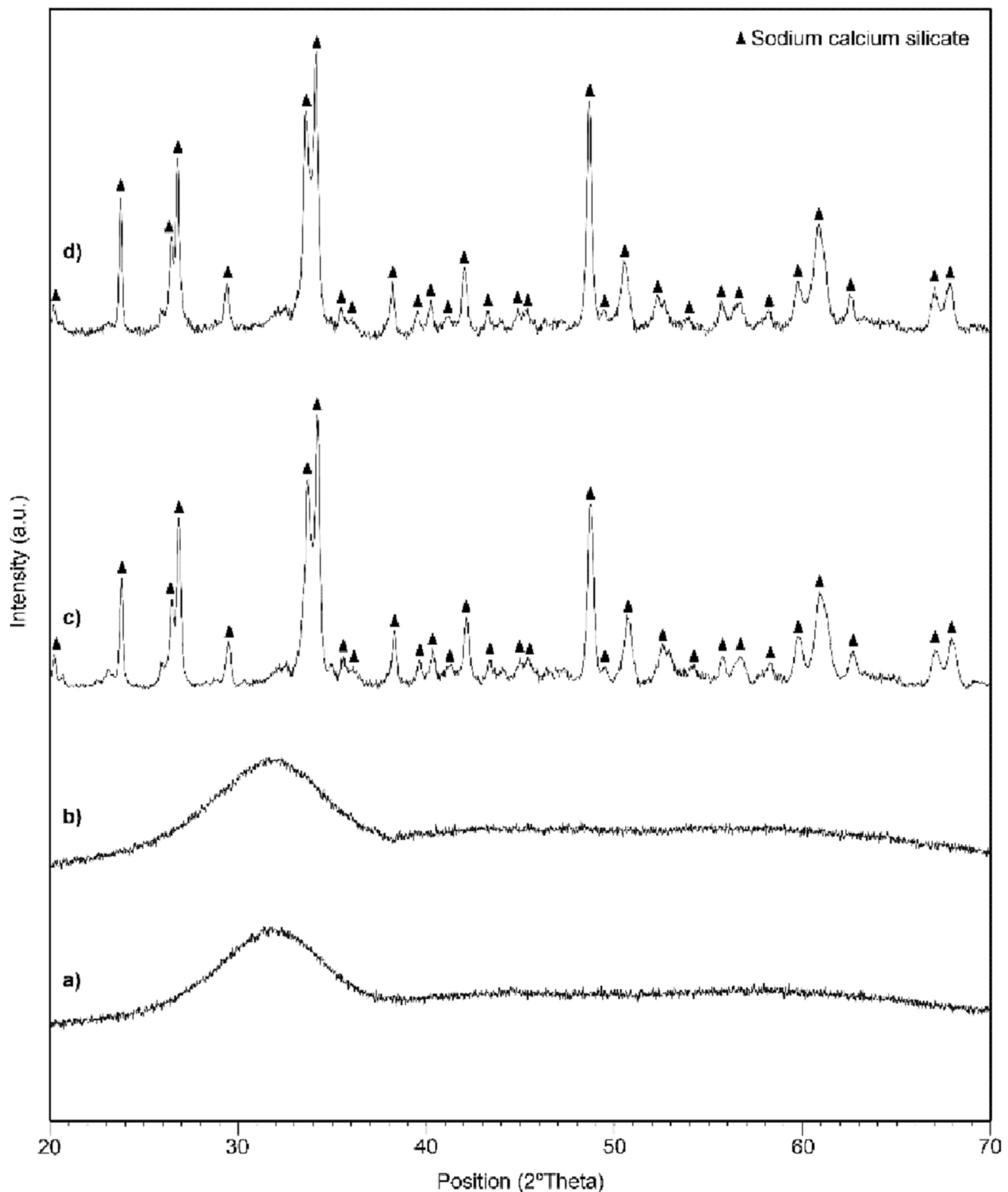


Fig. 8. X-ray spectra acquired on the samples as-sprayed: a) reference and b) agglomerates and after post-thermal treatment at 725 °C: c) reference TT and d) agglomerates TT.

The cross-section of the HCA layer formed after fourteen days of immersion can be observed in Fig. 10. After this period, a continuous layer (light grey) is formed throughout the surface of the coatings. For the reference, agglomerates and bilayer coatings, a thicker HCA layer was formed, with a thickness of $10 \pm 2 \mu\text{m}$, $10 \pm 2 \mu\text{m}$, and $9 \pm 1 \mu\text{m}$, respectively. The thickness of the HCA layer formed onto the surfaces of

the agglomerates TT and blended coatings reached lower values, $7 \pm 1 \mu\text{m}$, and $7 \pm 2 \mu\text{m}$.

The results of the cross-sections are in agreement with the SEM images in Fig. 9. The fast HCA layer growth for the reference, agglomerates, and bilayer coatings is corroborated. Furthermore, in these cross-sections, it is also possible to appreciate a significant internal porosity

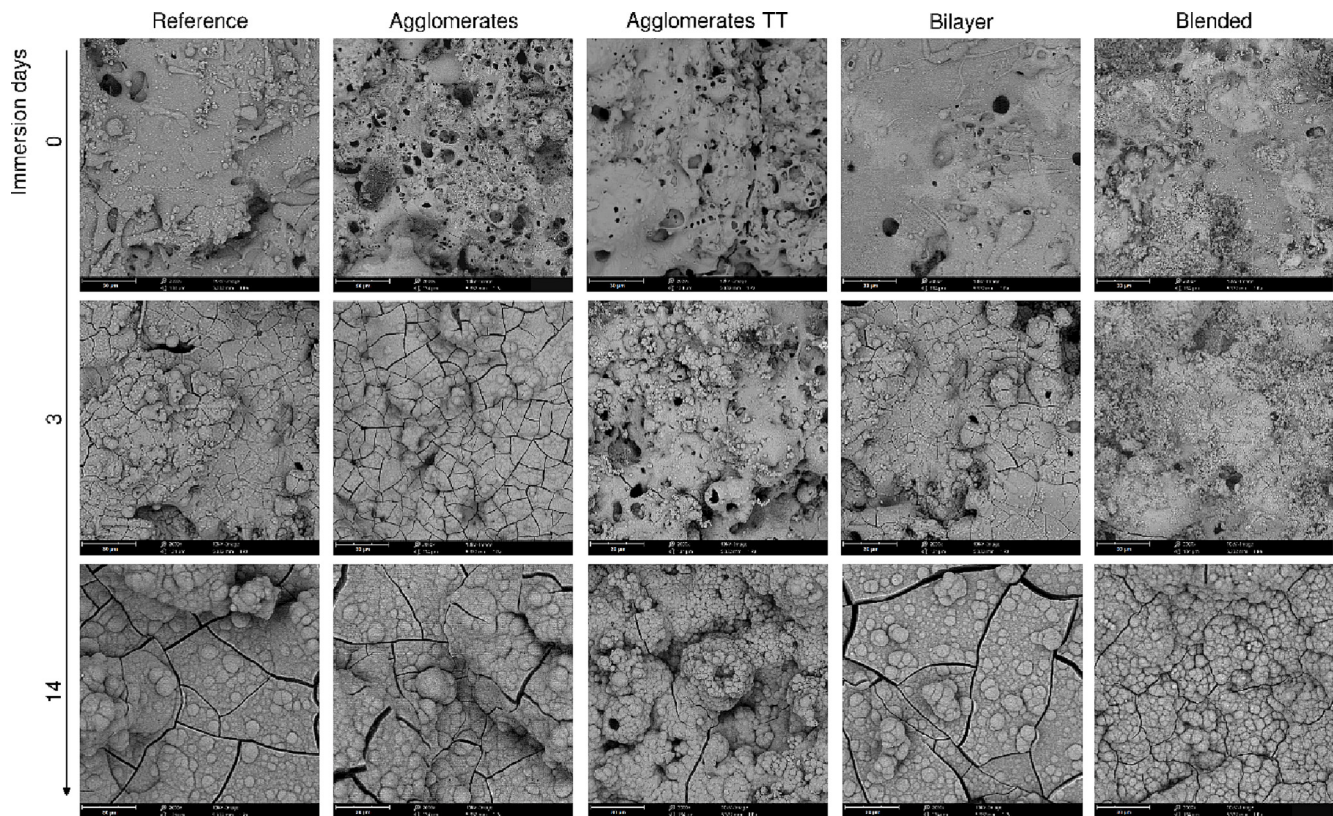


Fig. 9. SEM images of the samples without immersion and after soaking in HBSS for different times: after three and fourteen days.

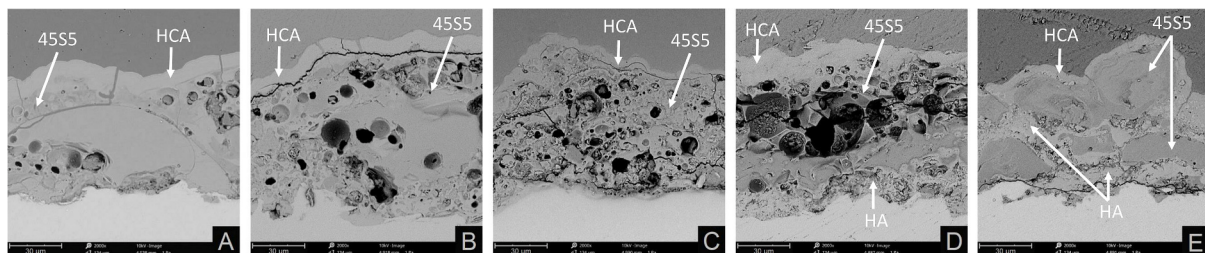


Fig. 10. Cross-section micrographs showing the HCA layer after fourteen days of immersion in HBSS: a) reference, b) agglomerates, c) agglomerates TT, d) bilayer and e) blended.

in the reference, agglomerates, agglomerates TT coatings, and the upper layer of the bilayer coating is entirely made of glass. In contrast, the HA layer of the bilayer coating and the blended coating present a dense microstructure after deposition.

As expected, due to the materials composing the coatings, the different strategies studied give rise to bioactive coatings. However, a significant difference has been noted in the kinetics of the formation of the HCA layer among these coatings.

3.4. Degradation assessment

The degradation rate and the ion release of bioactive materials are strongly linked to their osseointegration ability. The designed coatings' degradation behavior was evaluated to understand their biological capabilities further. The degradation of the coatings was characterized by the weight loss and ionic dissolution of the samples at different periods after immersion in physiological fluid and by the pH values recorded in the solution after the test. The percentages of weight loss of the samples are illustrated in Fig. 11.

For all the analyzed coatings, an increase in weight loss was observed

over time, with a rise in shorter periods and a slight tendency to stabilize in the latter. Agglomerates coatings reveal the highest weight loss rate. The authors suggest that it can be explained by the large surface area of the coating exposed to the solution and by the high surface porosity, as can be observed in Fig. 9. In particular, the agglomerates TT coatings show a significant reduction in weight loss compared to the agglomerates coatings that have not been thermally treated. This result can be explained by the crystalline phase generated from the heat treatment, giving rise to a more ordered and less reactive structure in the coating. This behavior was observed previously in our study [15], where bioactive glass coatings formed by non-agglomerated powders suffered less weight loss when thermally treated. Reference and bilayer coatings exhibited an intermediate result, and similar behavior was expected for these coating types since the top surface of both coatings had the same characteristics. In both cases, the surface was less rough and porous than agglomerates, which may explain the observed lower reactivity. Finally, blended coatings had few reactivities, with a similar result to the agglomerates TT. In the case of blended coatings, the lower weight loss can be explained by the presence of both HA and glass on the surface. In particular, HA regions are less reactive and cause less material release

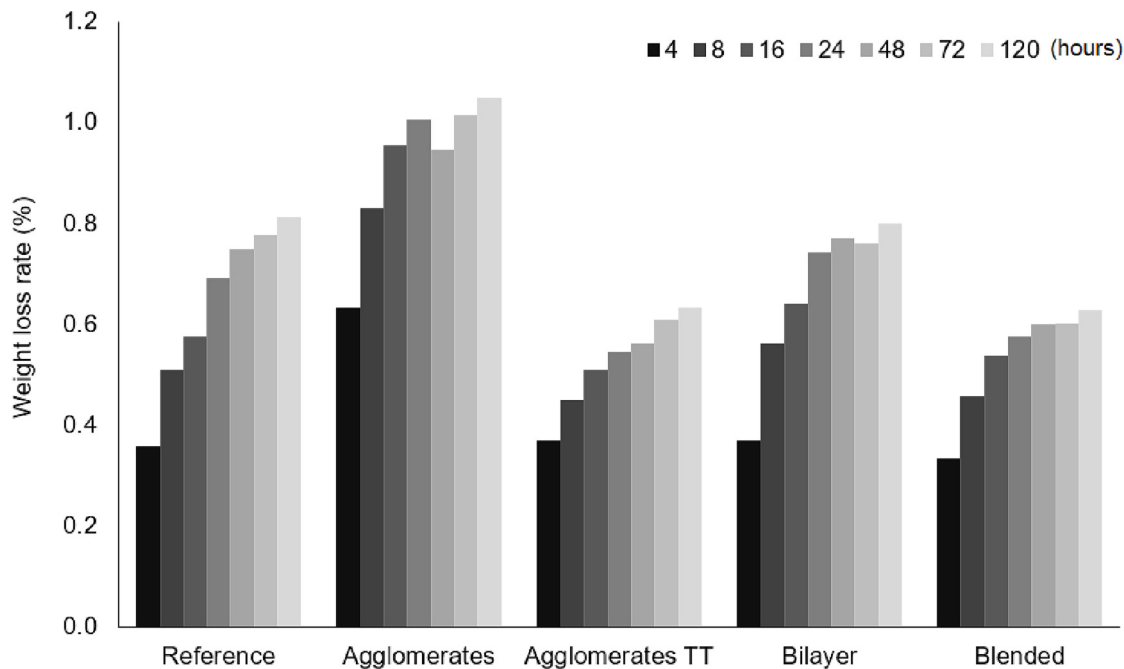


Fig. 11. The weight loss rate of coated samples after soaking in Tris-HCl solution for different periods (4, 8, 16, 24, 48, 72, and 120 h).

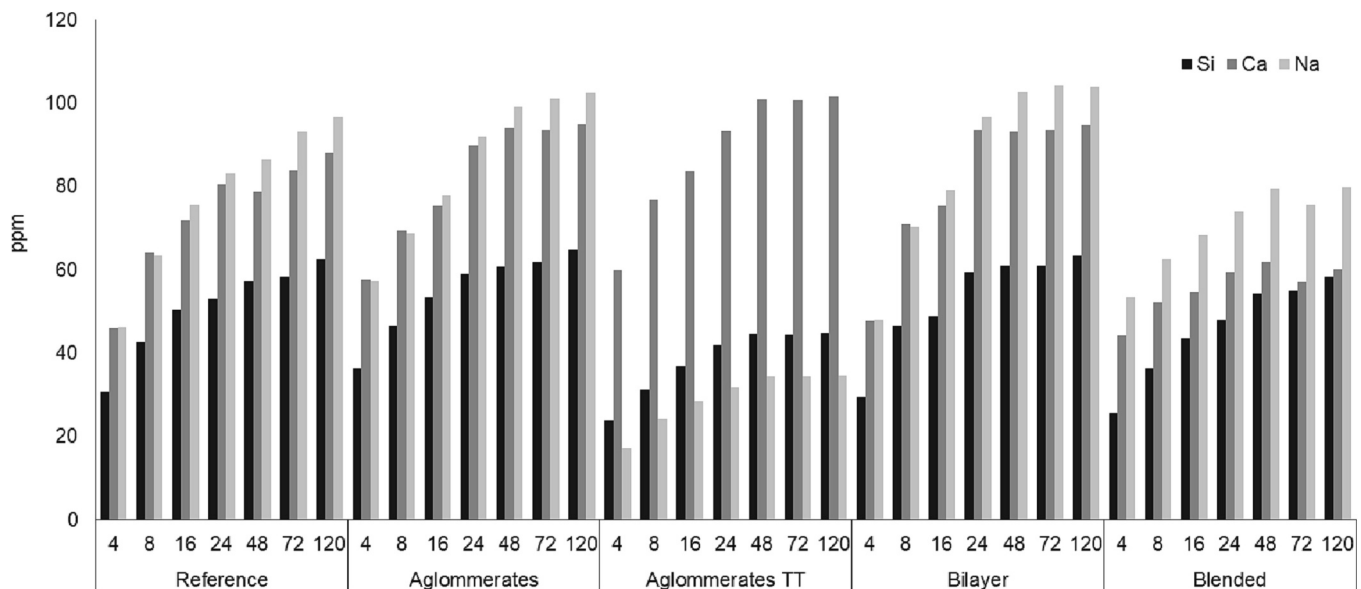


Fig. 12. Ion release after immersion in Tris-HCl solution at different periods (4, 8, 16, 24, 48, 72, and 120 h).

compared to a surface where only glass is exposed.

To further corroborate these findings, the analysis of ion release over time contributed to a better understanding of the degradation process of the different coatings. The results of the concentration of ions released during the degradation study are shown in Fig. 12.

For all the examined coatings, the release of silicon, calcium, and sodium ions increased with time, with the same trend observed in the samples' weight loss analysis. However, differences were observed in the ions released on each occasion. The first step in the dissolution of bioactive glass is the release of modifying cations [33]. It was clearly observed in the case of reference, agglomerates, and bilayer, where more calcium and sodium ions than silicon ions were detected in the solutions. These coatings showed the same behavior regarding the release of ions. In the first periods, a similar amount of calcium and sodium ions were

released. Moreover, these coatings showed that in the last periods, the amount of sodium released was slightly higher than that of calcium. The release of network-forming elements was lower for these coatings, and remarkably only silicon ions were detected in the solution due to the high contribution of silicon oxide (45 % by weight) in this glass composition and because of its low content of phosphorous pentoxide (6 % by weight in 45S5); for this reason, phosphorous release was not represented in Fig. 12. As expected, the change in the morphology of the feedstock powder did not affect the type of ions released. In contrast, the performance of the thermal treatment in the agglomerates TT coating resulted in a decrease in the number of ions released during the test. In this new structure, composed of an amorphous and a crystalline part, ions are released initially in the amorphous area since these elements are loosely bound in the structure. In that case, a change in trend was

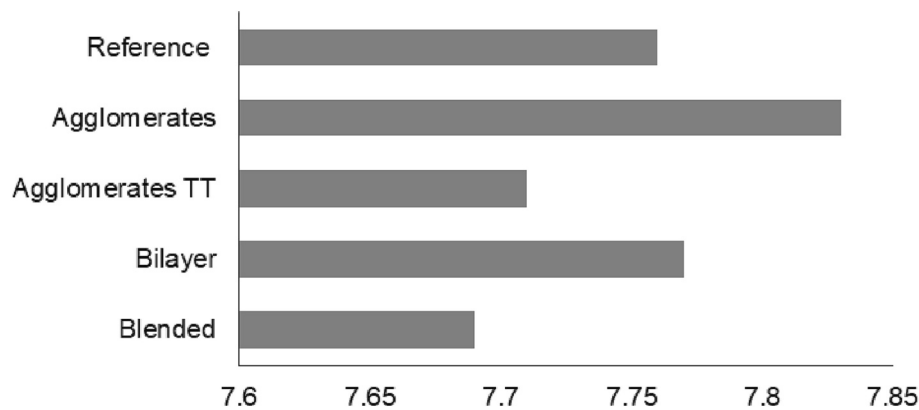


Fig. 13. pH value after immersion of samples into Tris-HCl solution for 120 h.

observed in terms of the elements released, as it approximately released three times more calcium ions than sodium ions, unlike the other coatings. This change was due to the crystalline phase $\text{Na}_6\text{Ca}_3\text{Si}_6\text{O}_{18}$ formed by the thermal treatment, where many sodium ions became part of this new phase. Furthermore, the incorporation of HA in the blended coating resulted in a minor release of elements but with an initial tendency similar to that of the reference, agglomerates, and bilayer. In particular, more sodium than calcium ions were released, and the difference increased for more prolonged periods suggesting that the HA of the surface may reabsorb some of the calcium ions released.

The results obtained by ICP analysis reflected different results for the different coatings studied. The amount of elements released was consistent with the weight loss measured, where reference, agglomerates, and blended coatings suffered the most significant weight loss and ion release.

After the period of 120 h, the ions released from the coatings caused a variation in the pH of the solution, which was initially 7.4, these results are shown in Fig. 13.

The recorded pH values revealed an increase after the test caused by the release of ions. In particular, the release of sodium and calcium ions causes an increase in the pH of the solution, while the release of silicon tends to reduce it. The pH results were consistent with the trend observed for the weight loss and the ion release of the coatings.

The results of the degradation study corroborated the findings related to the ability of the coatings to form an apatite layer, which occurs faster for the more reactive coatings (reference, agglomerates, and bilayer). Indeed, the characteristics that provide a greater bond strength are the same ones that cause a delay in the reactivity and, consequently, in the kinetic of HCA layer formation. Even so, all coatings can promote a bioactive response. Among the coatings evaluated in this part of the study, the coatings with the strongest adhesion presented the slowest bioactive behavior. These results prove that coating composition at the surface is crucial to the coatings' bioactive behavior.

Analyzing mechanical and biological properties, the more attractive candidates for use in implants are agglomerates TT, bilayer SH, and blended. Considering the manufacturing process, agglomerated TT coatings require a longer process, having to adapt the morphology of the powder and performing a post-treatment after the deposition process. Bilayer SH requires three steps in the plasma equipment, an initial stage of heating the substrate and the subsequent deposition of two different powders. The blended coating is formed by manually mixing the raw material powders in the same weight ratio. Thus, bilayer SH and blended coatings are easier to develop. This study verified that bioactive glass coatings with good adherence could be obtained, regardless of a certain reactivity.

4. Conclusions

Novel strategies for enhancing bioactive glass coatings' mechanical properties have been proposed.

Modifying the starting powders (morphology), incorporating HA, and applying heat before or after the coating deposition have successfully improved the bond strength of bioactive glasses. And the combination of various strategies has provided an even more significant increase in the adhesion to the substrate in most cases. The coatings that have reached the 22 MPa indicated by the standard contain crystalline phases, either because they contain HA or because of the heat treatment, which shows that it is hard for completely amorphous coatings to achieve the necessary mechanical properties.

The improved adhesion strength of the developed coatings is accompanied by a reduction in the bioactive response of the coatings, except for the coatings with glass with a completely amorphous structure on top.

After analyzing the set of results, the blended coatings would be the most promising candidate to improve the osseointegration process of current implants.

CRediT authorship contribution statement

Beatriz Garrido: Conceptualization, Methodology, Investigation, Writing- Original draft preparation, Revision.

Alejandro Martin-Morata: Investigation, Data curation.

Sergi Dosta: Conceptualization, Supervision.

Irene Garcia-Cano: Funding acquisition, Resources, Writing- Reviewing.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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