Mechanical and antibacterial behavior of multilayered geopolymer coatings on Ti6Al4V alloys

Alfredo Rondinella1,* Erika Furlani1, Lorenzo Dell’Antone1, Elia Marin2,3, Francesco Boschetto2,3, Francesco Sordetti1, Alex Lanzutti1, Francesco Andreatta1, Lorenzo Fedrizzi1, and Stefano Maschio1

1 Polytechnic Department of Engineering and Architecture, University of Udine, Via del Cotonificio 108, 33100 Udine, Italy
2 Ceramic Physics Laboratory, Kyoto Institute of Technology, Sakyo-ku, Matsugasaki, Kyoto 606-8585, Japan
3 Department of Dental Medicine, Graduate School of Medical Science, Kyoto Prefectural University of Medicine, Kamigyo-ku, Kyoto 602-8566, Japan

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ABSTRACT

Geopolymers are commonly used in a wide range of applications including binders into the building industry, production of refractory elements, filtration systems, low CO2 emission applications, etc. Their production can be performed either by acidic or alkaline formulation. In the last 15 years, however, they have been proposed also in biomedical applications for bone tissue regeneration. The aim of this work is the preparation of a thin and homogeneous geopolymer coating on a Ti6Al4V alloy in order to test their futuristic application as coating of prosthetic devices made with this metal alloy. Multilayered coatings were therefore produced by mean of dip coating with the aim of verifying which formulation, acidic or alkaline maximize adhesion. The morphological and chemical characteristics of the coatings were analyzed and adhesion of geopolymers to the substrate was investigated by scratch tests. Finally, a bacterial growth test was performed to verify antibacterial properties of the coatings.
**Introduction**

The term “Geopolymer” refers to a class of inorganic materials synthesized by reaction of an aluminosilicate powder in an alkaline or acidic environment [1–4]. The chemical reaction between the starting powder and the solution replicates an organic polymer-like condensation process in which the loss of a water molecule builds up covalent bonds between the mineral molecules [5, 6]. In order to obtain geopolymerization, starting aluminosilicate powders have to react within a suitable alkaline or acidic reagent solution [6]. These reactions normally occur at temperatures generally lower than 120 °C [7, 8] and lead to the formation of three-dimensional, nanoporous network structures with properties depending on the Si/Al atomic ratio [6, 7]. The resulting geopolymers might develop mechanical strength, chemical and thermal stability which makes them suitable for applications such as binders to be used into the building industry, production of refractories, thermal insulation devices, tiles and coatings [3, 9–14].

The commonly used organic coatings are susceptible toward external factors such as heat and UV rays [15, 16] which greatly reduce their performance in long time applications; conversely, geopolymer coatings are more stable over time [3]. In addition, their environmental impact and corresponding carbon emission are significantly lower [3]. The use of geopolymers aims to obtain long-lasting coatings with limited environmental impact.

In the last decade, geopolymers have been proposed as possible biomaterials [17]. The use of amorphous silicate-based systems has been proposed in the field of bone surgery due to their ability to bond the bone matrix [18, 19]. It has also been demonstrated that geopolymers surface display antibacterial properties, which are very important feature for biocompatibility [20].

The purpose of the present research work deals with the production of geopolymer-based coatings on Ti6Al4V alloy metal substrates by dip coating technique. Mechanical and antibacterial properties of multilayered alkaline or acidic geopolymer coatings, were tested in order to test their possible use in the production of artificial prostheses. The bacterial population used in this study was Staphylococcus epidermidis, a bacterial population naturally present on the skin which is also able to adhere to surfaces of catheters and prostheses,
contaminating them and requires removal of the contaminated device [21].

The dip coating process parameters have been optimized to obtain mechanically stable coatings which also retard/limit bacterial proliferation.

Materials and methods

Geopolymers formulations and dip coating process

A commercial metakaolin powder (Argical-M 1200, Imerys Refractory Minerals, Paris, France) was used as an aluminosilicate source during this work. The alkaline geo-synthesis was achieved by mixing a 42% wt. Sodium Silicate (Na2SO3) solution (F.Lli Mazzon, Vicenza, Italy), mixed with an 8M NaOH solution prepared using sodium hydroxide pellets 98% (Titolchimica Spa-Pontecchio Polesine, Ro-IT). Acidic reaction was achieved by the addition of Phosphoric Acid (H3PO4) 85% wt. solution (Titolchimica Spa-Pontecchio Polesine, Ro-IT).

The dip coating process was carried out on Ti6Al4V alloy disks (5 mm height and 25 mm diameter, Shinsei Co., Osaka, Japan) using a dip coating system (KSV NIMA Dip Coater Single Vessel, Biolin Scientific, Vastra Gotaland County, Sweden). Disks have been polished with a 220 grit Silicon Carbide sandpaper, using a grinder-polisher apparatus normally used for metallographic preparation (FORCIPOL 300-1V grinder-polisher, Metkon, Turchia). Ti6Al4V alloy disks were previously acid-etched, using Kroll’s reagent (commonly used to etch titanium alloys), in order to obtain a homogeneous surface with a thin and uniform oxide layer devoted to improve the adhesion of the coating. The solution was prepared by mixing 4 ml hydrofluoric acid (HF, 48% solution, Sigma-Aldrich, Missouri, USA), 12 ml nitric acid (HNO3, 69% solution, Sigma-Aldrich, Missouri, USA) and 184 ml distilled water for 5 min by a magnetic stirrer. The disks were soaked in the resulting solution and sonicated for 60 s. Etched disks were then sonicated for 5 min in distilled water followed by additional 5 min in acetone and finally oven dried for 30 min at 60 °C. After preparation, disks were fixed to a moving support connected to a dip coating system set with the following dipping parameters:

- Immersion and extraction rates: 100 mm/min;
- Contact time with the solution: 60 s.

Several formulations were tested in this work but, for the sake of brevity, only the best performing formulations for each type of geopolymer (acid/alkaline) will be reported. Compositions listed in Table 1, in fact, had both good mechanical properties and pore size distributions suitable for stimulating osteointegrative phenomena [4, 22–24].

Table 1 lists the main formulations employed during this research, using a custom system for labeling each type of formulation. Each label consists of a letter followed by a three digits number. The letter helps identifying the nature of the geopolymer (either “A” for acidic or “B” for alkaline) while the number corresponds to the amount of water (in grams) added during the geopolymerization. Dilute compositions were chosen in order to obtain thin layers, in view of the possible coatings to cover prosthetic devices.

During the early stages of this work it was observed that, regardless of geopolymers formulation and of metal surface treatment, the adhesion between metal substrate and acidic geopolymers is not good. For this reason, the first coating of all the samples, was performed by an alkaline geopolymer and a multilayered coating was built up. The coating structure is summarized in Fig. 1. The first layer, with formulation B146, acts as primer which develops a good adhesion with the metal substrate. Samples coated by the primer were shared into two sets: one half was coated with two more layers of alkaline-based geopolymer of formulation B110, which showed good adhesion and strength in previous tests. Coatings produced in this way will be referred from now on as “BBB” to indicate the presence of three “B” (alkaline) layers; the other half was coated with two more layers of acid-based geopolymer (A155) and will be referred in the manuscript as “BAA” to point out the presence of one “B” layer and two more “A” (acid) layers. After the deposition of each layer, the samples were cured for approximately 5 h at room temperature, followed by 24 h in an oven at 70 °C.

Sample characterization

The morphology of coated samples as well as their composition was analyzed by means of scanning
electron microscopy (SEM, ZEISS EVO 40 SEM, Zeiss Group, Jena, Germany) coupled with energy-dispersive X-ray spectroscopy (EDXS). The coatings cross section was also investigated in order to measure their thickness and to verify the interfaces homogeneity. Roughness values of the coating surfaces were measured by mean of surface profilometer (Dektak 150, Veeco, New York, USA).

**Mechanical testing**

Scratch tests were performed over coated samples to evaluate cohesion between metal and geopolymers, adhesive strength and failure modes of the ceramic layers on the metal substrates at room temperature. Tests were performed in accordance with the ASTM C1624-05 standard [25], in which a scratch is produced by means of a mobile indenter (Rockwell C type) moving along the surface of the sample at a constant speed and controlling the normal load applied. The type and degree of damage produced are subsequently evaluated along the scratch and associated with the normal applied load. The tests were made by a CETR UMT-2 Universal Micro Material Tester tribometer (Bruker, Massachusetts, USA), varying the load from 0 to 50 N, with a scratch length of 10 mm and a test duration of 90 s. Scratched samples were analyzed by scanning electron microscope (SEM). Data were also collected taking into account tangential force variation, and therefore not to neglect the changes of the normal load along the scratch.

**Antibacterial testing**

A solution containing a culture of gram-positive bacteria, Staphylococcus epidermidis, was used with a concentration of $1 \times 10^7$ CFU ml$^{-1}$. The bacterial culture was then transferred into 6-well plates in which the samples were present and brain heart infusion culture medium (BHI broth, Nissui, Tokyo, Japan) was added. Control wells were also used: positive controls, in which there was no sample but only the solution containing the bacteria and the culture medium, and negative control, which contained the culture medium and the saline solution without bacteria. These wells have been incubated for 24 h under aerobic conditions at 37°C. Colorimetric assays were performed using the Microbial Viability Assay Kit-WST (Dojindo Lab., Kumamoto, Japan). The assay uses an indicator, called WST-8 (a water-soluble tetrazolium salt), which is added to the samples together with a reagent. This reagent acts as an electron mediator, receiving electrons from viable bacterial cells and transferring them to the WST-8 indicator, which is consequently reduced to produce a water-soluble orange dye (formazan) with maximum absorbance at the 460 nm wavelength. The amount of dye produced, and consequently the absorbance of the solution is directly proportional to the number of viable microorganisms in each well analyzed. The obtained solutions were analyzed using the EMax microplate reader (Molecular Devices, San Jose, CA, USA).

| Reagent weight (g) | Ratios |
|-------------------|--------|
| MK | Na$_2$SiO$_3$ | NaOH | H$_3$PO$_4$ | H$_2$O | Si/Al | Si/P | Al$_2$O$_3$/Na$_2$O |
| B146 | 100 | 110 | 30 | – | 146 | 1.65 | – | 1.14 |
| B110 | 100 | 110 | 30 | – | 110 | 1.65 | – | 1.14 |
| A155 | 100 | – | – | 80 | 155 | 1 | 1.17 | – |

**Figure 1** Brief schematic of the multilayered coating structure.
Results

Coating characterization

The visual inspection of the samples shows no macroscopic difference in their appearance, as seen in Fig. 2. The coatings appear homogeneous and no macroscopic defects are visible on the surface.

Figure 3 compares the morphology of the coatings observed by mean of SEM, at different magnifications. Panels (a) and (b) of Fig. 3 show the surface morphology of the BAA sample. Several cracks in the coating are visible, even at low magnifications. The high-magnification picture shows that the geopolymer is present mostly as spherical particles.

The BBB coating is shown in panels (c) and (d) of Fig. 3. Significantly fewer and smaller cracks are present in this case whereas geopolymer contains several particles having acicular shape. Figure 4a, b shows the cross section pictures for BAA coatings and BBB coatings, respectively.

The thickness of the BAA coating (72.3 ± 2.2 μm) is slightly lower than that of the BBB coating (95.1 ± 1.6 μm).

The first layer shows good adhesion to the substrate in both cases, no detachments or voids can be observed. The three layers exhibit good adhesion and appear stuck together, although interfaces are still visible. It is also observed that the geopolymeric layers contain some porosity ranging in size from a
few hundred nanometers to few micrometers. Inclusions of unreacted metakaolin powder are also visible within geopolymeric material, especially in the BAA coating.

Results from the scratch tests on the BAA coating can be seen in Fig. 5. Panels (a) and (b) show the images obtained by means of secondary electrons of the scratched sample. A great number of particles, probably due to the detachment of fragments from the coating during the scratch test, are visible on the sample surface. The trace left by the penetrator is clearly visible and may be easily identified; in addition, it may be pointed out that the coating is removed only along the scratch and does not show fractures or detachment of fragments in the adjacent areas. Figure 5c, d shows the images seen in (a) and (b) obtained in backscattered electron signal. As seen from the scratch analysis in (a) and (b), the coating exhibits failure at the interface with the substrate even for small loads. Exposure of the substrate (highlighted by brighter color in the backscattered images) already occurred in the initial scratch path (panel (c)), at about 1.17 mm from the beginning of the test, for a value of about 7.5 N of the normal load Fz.

Figure 6 shows the surface of the sample made with alkaline-based geopolymer coating containing the scratch produced by the scratch test. Panels (a) and (b) represent the images of the sample obtained by SEM using secondary electrons while panels (c) and (d) show the same images as (a) and (b) obtained with the backscattered electron signal. As for the BAA coating, several particles are visible on the sample surface, probably due to the detachment of coating fragments even if their amount looks lower if compared to the previous case. The analysis
of pictures in panel (c) and (d) shows that no substrate exposure is observed up to the final part of the scratch.

A slight coating removal occurred at about 7.8 mm from the beginning of the test, but substantial coating removal with substrate exposure falls only at about 8.5 mm from the beginning of the scratch; from here on, the substrate is relatively well visible, although some dark areas are present indicating that part of the coating has not been removed, particularly in the scratch walls. The load required to break the coating and expose the substrate was about 40 N.

The results obtained from the absorbance of the solutions in the wells (colorimetric assay), measured after 24 and 48 h of incubation, are represented in Fig. 7. In particular, A indicates the values to the acid-based coating (BAA), B those relative to the alkaline-based coating (BBB), (+) and (−) are referred to the positive and negative control, respectively. It can be observed that the presence of the coating

![Figure 6 SEM pictures taken on the BAA coating after scratch tests: a start and b end of the scratch acquired with secondary electrons; c start and end d of the scratch acquired with backscattered electrons.](image)

![Figure 7 Colorimetric test of bacterial growth.](image)
(either BAA or BBB) influences the bacterial colony growth. The OD values for positive control (+) are about 1.5 after 24 h and about 3 after 48 h, showing a significant increase in the number of living bacteria. The phosphate-coated sample (A) shows an opposite trend. The OD value decreases from about 1 to less than 0.5 from 24 to 48 h given that the number of viable bacteria decreases. The well containing the alkaline-based geopolymer coated specimen (B), on the other hand, shows an increase in the number of viable bacteria over time, which, however, was significantly slowed down compared to the positive control. In particular, the measured absorbance value goes from about 0.2 at 24 h to slightly more than 0.5 at 48 h. In both cases, the maximum number of living bacteria in the wells is significantly lower than that of the positive control at 48 h.

**Discussion**

Visual inspection of the coatings, displayed in Fig. 2, showed no macroscopic differences between the BBB and BAA samples as their roughness values are not statistically different. Either type of coating appears well bonded to the substrate. A more detailed inspection, performed by mean of SEM analysis, showed several morphological differences in the two types of coatings. The BAA samples show a large number of micro-cracks and many geopolymer particles develop a spherical shape (cf. Fig. 3a, b) while the BBB samples contain fewer cracks and many particles display acicular geometry. Crack formation in geopolymer production is a well-known process due to shrinkage phenomena that occur during water evaporation [26, 27].

The difference in particle geometry observed between Fig. 3b and d samples could be due to different chemical attacks in the acidic and alkaline reaction. It is widely known that metakaolin powders particles have lamellar structure [28, 29]. It is generally accepted that the acid-activated geopolymerization is faster than the alkali-activated one; conversely its higher reaction rate limits the amount of reactive metakaolin. It follows that in the former several metakaolin particles remain unreacted and maintain their original shape and dimensions, in the latter most of the original metakaolin particles are dissolved, but their relic remains clearly visible. The difference in reaction types and rates could explain the higher presence of unreacted metakaolin in the BAA coating sections compared to the BBB coating observed in Fig. 4.

Cross sections images also revealed a slight difference in thickness (about 20 µm) between the two coatings. The reason is due to the different dilution of the different layers. The A155 layers, in fact, contain an amount of H2O which is always higher than the one in alkali layers. This lowers the viscosity of the mixture and causes the deposition of less geopolymer and more water on the surface of the sample. Since the water is then removed during curing, this causes a greater shrinkage phenomenon in the BAA coating, as also suggested by Temuujin et al. [30].

The scratch test results for BAA and BBB coatings showed a clear difference in adhesion. The secondary electron images of the BAA sample in Fig. 5a, b show numerous debris probably due to coating removal by the scratch. The backscattered electron images in panels (c) and (d) show that clear areas, i.e., those where the titanium alloy is exposed, are visible almost along the entire scratch because, even at low loads, the BAA coating is removed from the substrate. The results on the BBB sample, on the other hand, show greater adhesion with respect to the other type of coating. In fact, the amount of debris removed from the sample is significantly lower and amount of uncovered area is limited to the final part of the indentation. The difference in performance is probably due to the higher amount of unreacted metakaolin visible in the BAA samples. In both cases, the material is removed by the scratch, but not from the surrounding areas therefore showing that the coatings are well bonded to the substrate, especially in the BBB sample where considerable coating deformation can be observed due to a sufficient toughness.

The critical load value recorded for the BBB coating (40 N) is a more than acceptable value for this type of application. In the work of Zanocco et al. [31], a silicon nitride (Si3N4) coating for biomedical applications was produced on the same type of substrate using the same ASTM reference standard [25]. In that
research, the critical load target required for the specific application (the same as the present work) was 20 N. Although the Si₃N₄ coating’s test upper load limit was 25 N, it is possible to say that the BBB coating fully exceeds the requirements dictated by the application and is in line with the mechanical properties of a known, high-performance material.

The antibacterial properties are shown in Fig. 7. Data analysis in the graph shows that in the BAA sample, after 24 h of testing, there is substantial adhesion of bacteria to the sample surface comparable to that obtained in the positive control, although slightly lower. After 48 h, however, the number of live bacteria drops considerably and the OD value drops to about 1. In the BBB case, the number of live bacteria adhered to the surface is much lower than in both the positive control and the BAA sample. After 48 h, the number of live bacteria has slightly increased but still remains significantly lower than in the positive control. Therefore, it can be hypothesized that the BAA geopolymer performs a bactericidal action on the \textit{S. epidermidis} population while the BBB geopolymer simply hinders its adhesion.

There could be two possible reasons behind this difference and both are due to geopolymeric surface chemistry. The presence of residue Hydroxyl groups (OH) of geopolymers has been proved in a previous work [23]. However, the amount of OH groups strongly depends on the geopolymer formulations. The coatings two outermost layers, B146 and A155 for BBB and BAA coatings, respectively, will have different amounts of OH groups bound to the surface related to different reactants and different amounts of H₂O used during mixing.

Hydroxyl groups could have exerted an antibacterial effect either due to their interaction with the bacterial membrane [32, 33] or by having different effects on the local pH developing during the bacterial proliferation. It was already proved that geopolymers are stable during immersion in water [23] but it cannot be excluded that the peculiar chemical composition could alter pH locally affecting bacterial proliferation.

Conclusions

In this work, multilayered geopolymer coatings on Ti6Al4V substrates were produced in order to test their adhesion and antibacterial properties. The results obtained from the synthesis of geopolymers showed that a suitable surface preparation, in this case etching in Kroll’s solution, is always required to generate a sufficiently adherent coating. Due to the poor adhesion of acidic geopolymers to Titanium alloy, an alkaline-based primer was used as the base of the multilayer coatings. Mechanical and antibacterial characterization of the coating showed that:

- BBB and BAA coatings appear compact upon visual inspection but show the presence of cracks due to shrinkage, especially in the BAA samples;
- Acidic formulations have lower reactivity than alkaline formulations, causing different particle morphology at high magnifications and more unreacted metakaolin within the geopolymer;
- The BBB coating is found to adhere well to the substrate, as opposed to the BAA coating, which is removed even for low loads during the scratch test, probably also due to unreacted material;
- Both coatings slow bacterial growth, although the mechanism employed is different.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical standard This article contains no animal or human studies conducted by any of the authors.
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