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Grafting of gallic acid to metallic surfaces

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Abstract

The protection against bacteria, oxidation and corrosion is crucial for metals. Natural molecules can offer numerous of these properties, however they are poorly explored for the surface modification of metals. Gallic Acid (GA) was selected as model molecule for polyphenols to investigate the mechanisms involved in its grafting to the metallic surfaces. Ti6Al4V, AISI-204-Cu and AISI-304 stainless steels were used as substrates. GA solutions were prepared in different media (ultrapure water, TRIS/HCl buffer, TRIS/HCl buffer containing Ca^{2+} ions) to explore the role of the ionic composition and pH in the GA bonding ability to metallic substrates. Solutions were analyzed by means of UV and FTIR spectroscopies. The samples were characterized by means of FTIR spectroscopy and the Folin&Ciocalteu tests to evaluate GA presence and activity. Surface wettability was also evaluated.

GA was effectively grafted to all the surfaces maintaining its redox activity. FTIR and wettability tests confirmed its presence on the modified surfaces.

A crucial role of pH and Ca^{2+} presence in solutions was demonstrated and correlated to the formation of coordination compounds in solution and at the metal surface. It was observed that the surface chemical composition and the presence of functional groups affect the molecular grafting ability.

Graphical abstract

Keywords: metallic surfaces; gallic acid; surface functionalization; polyphenols; titanium; steel

Introduction

Natural polyphenols are gaining increasing interest in many applications because of their peculiar properties, such as the action against oxidation, inflammation, cancer and bacteria [1-3]. Moreover, they can be obtained as high added value molecules from some industrial byproducts (e.g. food and wine production) supporting a sustainable use of the resources.

Gallic Acid (3,4,5-trihydroxybenzoic acid, henceforth GA) is a simple molecule, belonging to the polyphenol family, present in many plants (e.g. grapes and tea) as well as in foods and beverages [4, 5]. It is often used as a standard reference for the quantification of the polyphenols (e.g. in the Folin & Ciocalteu test) [6] and it possesses numerous properties of interest for several applications (e.g. antioxidant, antibacterial and anticancer) [7-9]. It can be considered a good model molecule for polyphenols as well as an interesting compound for its intrinsic properties.

Numerous studies on its behavior as a pure molecule, in addition to some attempts of its coupling with materials for biomedical applications have been reported in the literature. For example, GA was coupled with chitosan in order to improve its antioxidant ability [7] and with gold nanoparticles to enhance the antibacterial activity [8]. Moreover, the authors successfully grafted GA to various bioactive glasses [10, 11, 12] and to bioactive titanium [13] for bone contact applications.

The interest for GA and polyphenols is not limited to the biomedical field; in fact antioxidant and antibacterial activities have been investigated in the food preservation context [14], their ability to bind proteins for the development of innovative surfaces for sensing and catalyst applications has been explored [15] and a possible corrosion protection effect on steel surfaces has been cited [16, 17].

In this context, the possibility to graft GA and polyphenols on metallic surfaces appears an interesting opportunity to confer the peculiar properties of polyphenols (e.g. antioxidant, antibacterial and corrosion protection) to the metal surface. GA and polyphenols can substitute some potentially toxic compounds (such as the disinfectants and cleaning products [18, 19]) with the natural ones. This environmental friendly approach is extremely promising for the industrial standpoint.

The aim of the present research work is the investigation of the ability and mechanism of grafting of GA on some metallic surfaces. The Ti6Al4V alloy, polished and chemically treated to obtain a nanotextured oxide layer rich in OH groups, as well as 304 and 204-Cu stainless steels have been considered as substrates in order to explore metals of interest in different applications, as well as surfaces with different surface chemical composition and functional groups. The solutions of GA have been prepared for the functionalization process in different media (ultrapure water, TRIS/HCl buffer and TRIS/HCl buffer added with CaCl_2) in order to investigate the role of pH and the ionic composition on GA grafting ability to metallic surfaces. In fact, in a previous work [13] the authors found a crucial role of pH (7.4) and the Ca presence in GA binding to the titanium surfaces.

The GA solutions were analyzed by means of UV and FTIR spectroscopies in order to investigate the chemical state of the GA molecule in the different media. Different techniques have been used in order to verify the presence and reactivity (redox activity) of the grafted GA on the functionalized metallic surfaces: FTIR spectroscopy, Folin & Ciocalteu test (adapted to the solid surfaces), and contact angle measurements.

Materials and methods

Samples preparation

The Ti6Al4V samples (discs with 10mm diameter and 2 mm thickness) were obtained from cylindrical bars (ASTM B348, Gr5, Titanium Consulting and Trading) and Stainless steels 304 and 204 Cu samples (square samples 1x1 cm area, 2mm thickness) were obtained from plates (Outokumpu Spa) by means of automatic cutting (ATA Brilliant 220, with abrasive alumina wheel). All specimens were polished with SiC abrasive papers up to 4000 grit. Samples will be named Ti6Al4V – MP, SS 304 and SS 204-Cu.

After polishing, the samples were washed once for 5 min in acetone and twice for 10min in ultrapure water with an ultrasonic bath and let it dry in air.

A part of the Ti6Al4V samples underwent a patented chemical treatment (hydrofluoric etching followed by hydrogen peroxide oxidation) [19, 20] in order to develop a surface nanotextured oxide layer rich in hydroxyl groups, potentially useful for biomolecular grafting [13, 21]. The chemically treated Ti6Al4V samples will be named Ti6Al4V – CT from now on.

Preparation of the solutions of Gallic Acid

Gallic Acid 8GA , 3,4,5-Trihydroxybenzoic acid, 97.5–102.5% titration, G7384, Sigma-Aldrich, St. Louis, MO, USA) was dissolved in different media (ultrapure water, TRIS/HCl buffer and calcium chloride solution 292 mg/l in TRIS/HCl buffer solution) at 1 mg/ml concentration. Solutions will be named: GA (water), GA (TRIS/HCl) and GA (TRIS/HCl+CaCl₂). The media were selected in order to investigate the effect of pH and the ionic composition in the GA grafting ability to metallic surfaces. The Ca²⁺ ions were selected as allowable mediators for GA binding to metallic surfaces on the basis of a previous research of the authors [13].

The solutions were characterized by means of macroscopic observation of their appearance, pH measurements (Edge pH, HANNA Instruments), UV spectroscopy (UV-2600 Shimadzu) and Fourier Transformed Infrared Spectroscopy (FTIR, Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer).

Surface functionalization

Titanium samples underwent an UV-C irradiation (1h) before functionalization in order to activate the surface for grafting [13].

For all the substrates, each sample was soaked in the GA solution for 3h at 37°C in the dark. At the end of the soaking period, the samples were gently washed twice in ultrapure water and let it dry in air in the dark.

Detection of GA on functionalized surfaces

The presence of the grafted GA on the functionalized surfaces was investigated by means of Fourier Transformed Infrared Spectroscopy (FTIR, Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer) in ATR mode. This technique gives information on the functional groups exposed on the surfaces after GA grafting and is of interest in the investigation of the molecule orientation and grafting mechanisms.

The presence and activity of the grafted GA was measured on the metallic samples by means of the Folin&Ciocalteu method. This technique is widely used for the quantification of total phenols in a liquid

phenolic mixture by using GA as a standard and adapted by the authors to the analysis of the solid samples as described in previous works [11, 23]. In brief, each functionalized sample was soaked in 8 ml of ultrapure water and 0.5 ml of the Folin&Ciocalteu phenol reagent (2 M with respect to acid, Sigma Aldrich) and 1.5 ml of Na_2CO_3 (20% w/V) were sequentially added. After 2h, the samples were extracted and the absorbance of the solutions at 760 nm recorded with an UV spectrophotometer (UV-2600 Shimadzu). GA was quantified in accordance with a standard calibration curve [11, 23]. Since the test is based on a redox reaction, the results give information both on the amount and on the redox activity of the grafted molecule.

Surface wettability was evaluated through the measurement of the static contact angle by the sessile drop method (Kruss DSA 100), using ultrapure water as a wetting fluid. A drop (5 μl) of ultrapure water was deposited on the sample surface with a micro-pipette and the contact angle measured through the instrument software.

Results and discussion

The UV spectra, the appearance of the GA solutions in different media and the hypothesized chemical structures of the molecule are reported in Figure 1.

The solution of GA in water has an acidic pH = 3 and a colorless appearance (Figure 1a). The UV spectrum of the solution (Figure 1d) evidences a peak at 269 nm, typical of GA in acidic media [24] and consistent with its fully protonated form (Figure 1a).

The solution of GA in TRIS/HCl has a neutral pH = 7.4 (the physiological value) and the color of the solution turns to green (Figure 1b) due to the deprotonation of the carboxylic group [25] and to the possible presence of oxidized molecules (quinone form). The UV spectrum of the solution (Figure 1d) evidences the most intense peak at 259 nm and the appearance of two shoulders at about 338 nm and 443 nm which can be associated with the deprotonation of the carboxylic group, with the polymerization of GA molecules in solution [26] and with the presence of oxidized molecules (quinone) [17].

GA in TRIS/HCl solution containing Ca^{2+} ions has the same pH of the TRIS/HCl one (7.4, the physiological pH), but the color turns to blue (Figure 1c) due to the formation of a GA-metal ion complex [17]. The UV spectrum of the solution (Figure 1d) evidences the most intense peak at 259 nm, which presents a moderate shoulder if compared to the one of GA in water, and the appearance of a broad peak at about 640 nm, which can be associated with the formation of a GA-metal ion complex [24, 27]. Different gallic acid calcium complexes can be hypothesized (Figure 1c). The molecular structures are reported in the planar form for simplicity, but the stereochemistry of the GA complexes has not been investigated and is out of the scope of this work. Even if at pH 7.4 only the carboxylic group of GA is deprotonated (deprotonation of OH phenolic groups occurs at pH higher than 8.5) [25], the formation of a calcium gallate complex by means of the interaction between Ca^{2+} ions and gallic acid phenolic OH becomes possible due to the high stability of the formed complex. Moreover it should be underlined that the bonding of the Ca^{2+} ion to the phenolate moiety of the ligand molecule (gallate) protects gallic acid from oxidation. The significant reduction of the shoulders at about 338 nm and 443 nm in the GA (TRIS/HCl+ CaCl_2) UV spectrum (Figure 1d) supports this hypothesis.

Figure 1: Appearance, pH and the hypothesized chemical state of the molecule of GA in solution in water (a), TRIS/HCl (b) and TRIS/HCl+CaCl₂ (c) and UV spectra of the same solutions (d).

FTIR spectra of the GA powder and GA solutions in water, TRIS/HCl and TRIS/HCl+CaCl₂ media are reported in Figure 2.

Figure 2: FTIR spectra of GA powder and GA solutions in water, TRIS/HCl and TRIS/HCl+CaCl₂ media.

The spectrum of the GA powder is consistent with the results reported in the literature [28, 29, 30] with the main peaks at about 3500 and 3200 cm⁻¹, attributable to the OH stretching of the phenolic groups, and a characteristic fingerprint between 1800 and 550 cm⁻¹, which evidences signals at about 1700 cm⁻¹ and 1029 cm⁻¹, associated with the carbonyl group and the benzene ring respectively [30].

The spectra of the GA solutions in the different media are almost equal (no differences attributable to the medium can be evidenced by this technique), but are significantly different from the one of the GA powder. In particular, the disappearance of the fingerprint can be observed, together with a broadening of the signal in the 3200-3500 cm⁻¹ region. These modifications can be attributed to a partial polymerization of the GA molecules in the solution [26, 31].

In conclusion, we can assess that GA is present in all the solutions as partially polymerized (FTIR), but with deprotonated carboxylic groups and a higher degree of polymerization in the solutions at pH = 7.4 (UV, color of the solutions). Moreover, GA forms metal-ion complexes with Ca⁺⁺ if it is added in the solution (UV, color of the solutions).

The FTIR spectra of the metallic surfaces before and after grafting with GA are reported in Figures 3 and 4.

Considering that the used functionalization procedure can develop on the metallic surfaces a thin (monomolecular) layer of GA [13], the FTIR signals, which are acquired within a penetration depth of at about 1 μm, are of moderate intensity because they are affected by the substrate presence.

On the polished Ti6Al4V surfaces, the signals accounted for the grafted molecules of GA are the small peaks respectively at about 2900 cm⁻¹, attributable to the C-H bonds, at 1735 cm⁻¹, attributable to the C=O bonds and at 1264 cm⁻¹ attributable to the C-O bonds [17, 28, 29, 30]. These peaks are absent on the substrate before functionalization (Ti6Al4V-MP) as well as on the sample functionalized in water (Ti6Al4V-MP GA (wat)), while are detected on Ti6Al4V – MP GA (TRIS/HCl), Ti6Al4V – MP GA (TRIS/HCl+CaCl₂). It can be

concluded that the polished surface of this material has a low grafting ability, and the presence of the deprotonated carboxylic groups on GA and Ca^{2+} ions in the solution is mandatory for grafting.

On the chemically treated Ti6Al4V samples, the signals accounted for the grafted molecules of GA are the broad band between 3000 and 3600 cm^{-1} on Ti6Al4V – CT GA (water) and Ti6Al4V – CT GA (TRIS/HCl+ CaCl_2) and can be attributed to the OH groups, as the signal at 1058 cm^{-1} , while the peak at about 1600 cm^{-1} can be associated with C-C bonds [17, 28, 29, 30]. All the signals attributable to the grafted GA are much more intense on Ti6Al4V-CT than the same signals on the MP substrate: this evidence a higher ability for grafting of the Ti6Al4V alloy after the surface treatment. This effect can be explained considering that Ti6Al4V-MP has very few surface functional groups, while Ti6Al4V-CT has a much higher density of OH groups [19]. No evidence of the presence of the grafted GA is detectable on Ti6Al4V-CT (TRIS/HCl) which has a spectrum analogous to the substrate before functionalization (Ti6Al4V-CT). This effect can be explained by considering that the OH groups on Ti6Al4V-CT have a strong acid strength [32] and they are fully deprotonated at the physiological pH: the GA molecule deprotonated and negatively charged has no grafting ability on the negative charged surface of Ti6Al4V-CT (as observed on Ti6Al4V-CT (TRIS/HCl)), while GA has an electrostatic attraction for the surface in the protonated state (Ti6Al4V-CT (wat)) or like a complex with the Ca^{2+} ions (Ti6Al4V-CT (TRIS/HCl+ CaCl_2)).

On the steel surfaces (Figure 4), a signal accounted for the grafted molecules of GA is the broad band between 3000 and 3600 cm^{-1} which can be slightly detected on SS 304 GA (TRIS/HCl) and SS304 GA (TRIS/HCl+ CaCl_2) and attributed to the OH groups [17, 28, 29, 30]. A broad band around 1600 cm^{-1} can be observed on SS304 GA (TRIS/HCl+ CaCl_2) and SS 204 GA (TRIS/HCl+ CaCl_2) and it is associated with the C-C bonds [17, 28, 29, 30]. Moreover, a signal at about 1060 cm^{-1} , attributable to the OH groups [17, 28, 29, 30], can be detected on SS 304 GA (TRIS/HCl) and SS304 GA (TRIS/HCl+ CaCl_2) and on all the GA grafted SS 204-Cu surfaces. It can be concluded that also on the steels surfaces the Ca^{2+} ions are able to increase the grafting ability of GA giving much more evident FTIR signals.

A signal at about 1730 cm^{-1} , as the one observed on Ti6Al4V – MP GA (TRIS/HCl) and Ti6Al4V – MP GA (TRIS/HCl+ CaCl_2) and attributed to C=O bonds, is also visible on the steel surfaces; however in these cases it is also present on the bare material. This phenomenon can be associated with the interaction of steel surface with air, as reported in [33] or with an instrumental artifact and it is not significant for the evaluation of the grafting of GA.

Figure 3: The FTIR spectra of the substrates and GA-grafted titanium surfaces: (a) polished Ti6Al4V, (b) chemically treated Ti6Al4V

Figure 4: FTIR spectra of the substrates and GA-grafted steel surfaces :(a) SS 304, (b) SS 204-Cu

The results of the Folin&Ciocalteu test are reported in Figure 5.

Figure 5: Redox activity of the GA grafted surfaces (Folin&Ciocalteu test)

The amount of GA detected by the Folin & Ciocalteu test results negligible on the surface polished Ti6Al4V samples while it increases on the chemically treated Ti6Al4V and particularly when the GA solution is prepared in a TRIS/HCl buffer added with CaCl₂. This behavior is in agreement with the FTIR data and can be explained by considering that the Ti6Al4V – CT samples are rich in OH groups, which are suitable for GA grafting, and that the Ca⁺⁺ ions can mediate the bonding between the Ti-OH groups and GA molecules through the formation of a heterogeneous ternary metal-ion complex, as previously reported by the authors [13]. All the here hypothesized Ca-gallic acid complexes are negatively charged and can interact with the negatively charged metallic surface through the formation of ternary complexes at the surface. A considerable amount of GA has been detected on the steel surfaces and it increases when grafting is performed in TRIS/HCl buffer or TRIS/HCl buffer added with CaCl₂. A higher affinity of GA with the steel surfaces, compared to the titanium ones, can be explained by considering the high affinity of GA with the iron ions [27, 28]. The role of calcium in this interaction, can be similar to the one described for titanium surfaces, but it should be investigated more in depth in the future.

The Folin & Ciocalteu test is a further confirmation of the success of GA grafting on the metallic surfaces, moreover it underlines that GA maintains its redox activity after grafting. This point is of interest considering the exploitation of the GA properties on the metallic surfaces.

The results of the wettability tests are reported in Figure 6.

Figure 6: Wettability of bare and GA grafted metallic surfaces.

A reduction of the water contact angle (increase in wettability) can be observed on all surfaces after GA grafting. A decrease in the contact angle can be associated with the presence of the OH groups, characteristic of the GA molecule. This phenomenon is particularly evident for Ti6Al4V – CT, probably because this surface has a specific surface chemistry and exposes function groups (OH) acting as a strong acid: this can result in a specific orientation of the grafted GA molecules with a higher exposition of their hydrophilic domain.

The wettability measurements appear a useful technique for the determination of the GA presence on metallic surfaces: it is simple, sensitive and able to evidence specific surface orientation of the grafted molecules. Moreover, wettability is a surface property of interest for several applications. In any case, the FTIR, UV and contact angle measurements must be used in a complementary way for a comprehensive understanding of the grafting process. The developed protocol allows a comprehension of the role on grafting of the surface chemistry of the substrate, the chemical state of the molecule in the solution, the presence of ions in the solution, the amount, surface distribution redox activity and orientation of the grafted molecule.

Summarizing the obtained results, gallic acid is in its fully protonated form in the acidic ultrapure water, its carboxylic group becomes deprotonated in neutral medium (TRIS/HCl) and possible partial oxidation occurs in these conditions (quinone formation). In neutral medium containing calcium ions (TRIS/HCl+CaCl₂) the formation of several different negatively charged calcium-gallate complexes can be supposed, with higher stability with respect to oxidation. A partial polymerization of GA molecules in all solutions has also been evidenced (UV, FTIR).

When these solutions are put in contact with metallic surfaces different interactions can be supposed.

In the acidic environment (pH=3) of GA (water) solution Ti6Al4V – MP and steels are negatively charged, because their isoelectric points are close to 4.5 [32, 34] while Ti6Al4V – CT is negatively charged (isoelectric point close to 2) [32]. In these conditions the electrostatic affinity between GA and Ti6Al4V – MP and steels is low while the one between GA and Ti6Al4V – CT is higher. This is fully confirmed by FTIR, F&C and wettability data for titanium surfaces. A certain grafting of GA on steels surfaces occurred also in water and it can be correlated with the high affinity of GA for iron [27, 28].

In the neutral environment (pH=7.4) of GA (TRIS/HCl) solution all surfaces are negatively charged and consequently do not have electrostatic affinity for deprotonated GA. In particular Ti6Al4V – CT presents a high amount of OH groups with a strong acid strength [32] and fully deprotonated at pH=7.4. This behavior can explain the worst results of GA grafting on Ti6Al4V – CT in TRIS/HCl solution, compared to the other substrates. As discussed before certain grafting of GA on steels surfaces (even higher than in water) can be correlated with the high affinity of GA for iron [27, 28].

In the GA (TRIS/HCL + CaCl₂) solution surfaces are still all negatively charged (pH=7.4) and GA is present in the form of negatively charged metal complexes (with various possible configurations). In this case an increased ability of grafting has been recorded (FTIR, F&C, wettability) on all materials and can be explained considering the formation of ternary complexes at the metallic surfaces (as reported by the authors in [13] for Ti6Al4V – CT) with Ca²⁺ as intermediate cation. The possible role of iron in this environment should be further investigated.

Finally it can be observed that the polymerization of GA in the various solution, evidenced in the present work, can have a role in the grafting ability, in fact, it has been reported that this phenomenon can reduce the solubility of polyphenol in solution and increase their ability to form coatings on material surfaces [35]. This point is of particular interest for the optimization of grafting condition and will be further investigated.

Conclusions

GA solutions have been prepared in different media (water, TRIS/HCl buffer and TRIS/HCl buffer added with CaCl₂) and characterized by means of UV and FTIR spectroscopies, in order to explore the role of pH and the ionic composition on the GA grafting ability. GA has a different chemical state and polymerization degree in the different solutions. GA has been successfully grafted on different metallic surfaces: Ti6Al4V polished and chemically treated, SS 304 and SS 204-Cu polished. Its presence has been verified by means of FTIR spectroscopy, Folin&Ciocalteu and wettability tests. A crucial role of the medium used for the preparation of the GA functionalization solution has been highlighted, evidencing an important action of the Ca²⁺ ions in the binding mechanisms. A crucial role on the grafting ability and on the orientation of the grafted molecules is also played by the surface chemistry of the substrate and the presence of functional groups on it. The grafted GA molecules effectively maintain their redox ability on the different metallic surfaces. Moreover, a protocol for the characterization of the modified surfaces has been developed for the first time. This work is the preliminary step for a future research on the surface modification of metals with natural molecules, which can be a green approach for the obtainment of smart functional surfaces for several applications.

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