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Hybrid and Composite Polymeric Coatings for Anticorrosion Protection of Metals

Abstract

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Abstract of the thesis

Objectives

The main objectives of the present doctoral thesis were the development and evaluation of multifunctional corrosion-inhibiting coatings of different chemical nature, tailored for specific metal substrates—mild steel, zinc, and titanium alloys.

1. Across all experimental series, a consistent objective was the establishment of the relationship between coating microstructure, inhibitor incorporation methods and their distribution within matrices, and the evaluation of their functional application and performance. The research aimed to clarify differences in substrate types, surface chemistry, and application areas, facilitating a focused evaluation of protective mechanisms across organic, silica-based, and titanium dioxide coatings.

2. Mild steel was selected as a model substrate for evaluating the organic coating systems. The focus was placed on coatings that are simple, readily accessible and compatible with industrial-scale manufacturing. As such, two distinct types of inhibitor-enhanced organic coatings were studied, namely (i) benzotriazole-doped organic paint systems (primer and undercoating) and (ii) tannic acid-modified polystyrene coatings. The objectives of the studies presented were to examine how the coatings composition influence adhesion, electrochemical behaviour, and the potential for cost-effective upgrades of commonly used organic coatings. Barrier integrity and corrosion performance of these coatings were thoroughly investigated.

3. Silica sol-gel systems were employed on zinc substrates using a range of inhibitors to further enhance corrosion resistance. Entrapment efficiency and corrosion behaviour were studied on mesoporous silica coatings impregnated with benzotriazole and cetyltrimethylammonium bromide. In parallel, compact silica films containing tannic acid at various concentrations were studied in long-term wet-dry electrochemical impedance cycles and characterised by spectroscopic, microscopic and physico-chemical methods. Both systems aimed to clarify how pore architecture and inhibitor integration influence hydrophobicity, electrochemical stability, and corrosion behaviour.

4. Titanium substrates were also studied, given their high bio-application rates. The aim of the presented studies was to develop sol-gel titanium dioxide coatings capable of delivering both corrosion protection and antimicrobial functionalities. Eugenol, a natural additive, was directly introduced into the titanium dioxide precursor and studied to elucidate further the incorporation method, anti-corrosive effects, and biomedical applicability. In a second study, silver nitrate was introduced into titanium dioxide coatings by incorporation into the precursor as well as by impregnation. The different integration methods compelled a comparative evaluation of their impact upon electrochemical behaviour and antimicrobial performance. Both studies provided deeper insights into the optimal design of effective bioactive implant coating systems.

Chapters 4 to 9 of the thesis present all the results obtained and the conclusions drawn from them.

I. Literature Review

1. Introduction

Corrosion is a natural process that implies a metal's chemical or electrochemical interaction with its environment, which can lead to its deterioration. Corrosion significantly impacts the durability of any type of metallic structure in the long term. Metal corrosion substantially differs from other types of erosion or mechanical damage, as it can potentially lead to thinning, cracking or delamination of a metal structure or equipment [1–3]. To mitigate its effects, cathodic and anodic protection methods, production of metal alloys and several minimisation and optimisation techniques have been studied and elaborated to date [4].

1.1. Barrier Coatings

Barrier coatings are the most widely applied prevention methods. Chromate conversion coatings very widely known and applied systems are now no longer applied because of the banned and toxic Cr (VI) contents [5, 6].

BSAS ceramic materials, and metal-oxide based coatings are part of the inorganic coating family and serve as the basis for modern inorganic systems [7–9]. Two of the most outstanding inorganic coatings are silica (SiO_2) and titanium dioxide (TiO_2). The unique properties, preparation by the sol-gel method, and inertness of these two barrier coatings have enabled their extensive application in various industrial and biomedical fields [10, 11].

Organic coatings are among the oldest corrosion-mitigating coating types. These are widely applied in the automotive, aviation, marine, and construction industries. The oldest and most commonly applied of these are organic paints. Paints can be of water or solvent base. Both are beneficial in different settings and for different purposes, as such, still justifying the use of solvent-based organic coatings regardless of their higher volatile organic content emissions [12, 13]. Other examples of organic coatings are organic polymer coatings, which are widely applied due to their malleability and customizability to conform with the application area and requirements [14]. The most commonly used and researched materials include epoxy resins, polypyrrole, polyurethane, and polytetrafluoroethylene (PTFE) coatings.

Hybrid coatings have gained significant interest because they combine the desirable properties of both organic and inorganic coatings, while also diminishing their individual weaknesses. These coatings can have an inorganic backbone with organic functionality or vice versa [15]. Silicon-based hybrid coatings are among the most popular types. These vary from the old-timer ormacers to the contemporary mesoporous hybrid SiO_2-ZrO_2 coatings loaded with organic inhibitors. Another prime example of hybrid coatings are Ti-based polymers, mostly used in biomedical fields (e.g. titanium dioxide and hydroxyapatite hybrids, TiO_2-HA) because of its high bioavailability. Organic-hybrids are based on an organic backbone doped with inorganic fillers and additives, showing improved thermal, mechanical and physical properties all offered by the inorganic materials [16–18]. Several studies have explored the hybridisation of epoxy coatings with various inorganic substances, including silica nanoparticles.

1.2. Corrosion Inhibiting Additives

Aditives used to improve anti-corrosion systems are known as corrosion inhibitors. These can present as fillers (commonly used in organic-inorganic hybrid coatings), which increase electrolyte pathways or additives displaying genuine inhibitory effects upon the corrosion process. Corrosion inhibitors exhibit their effects on the metal-solution interface, or by incorporation into the barrier coating matrix. Corrosion inhibiting additives exhibit their effects without affecting the structural integrity of the metal substrates to which they are applied [19].

1.3. Precursor Preparation Methods

Precursors of barrier coatings can be obtained in multiple ways, such as dispersion methods or the sol-gel technique. Each applied method is dependent on the coating materials used, and is customized to offer the appropriate corrosion protection. Dispersion methods, often seen in organic systems, imply the even distribution of solid nanoparticles within a coating precursor, leading to homogenous and uniform coatings [19]. Sol-gel, on the other hand, is more representative of inorganic substances. It is an advantageous technique because of its high purity, low thermal requirements, easy customisation and cost-effectiveness. It is based on the catalytic gelification process of a colloidal suspension, the sol. Its two main steps are hydrolysis and condensation, accompanied by gelation, polymerisation, drying and densification processes as well [20].

1.4. Coating Techniques

Coating application methods depend on the surface material, coating type and application area. Choosing the appropriate application method has the potential to significantly improve coating properties and prolong endurance as well as offering more appealing aesthetic features. The present study is focused on protective layers prepared by the sol-gel method and the dip-coating technique. Dip-coating is one of the oldest coating application methods, and is used in various fields. The technique relies on the careful and controlled submersion of a metal substrate into a precursor solution, which is then removed with a deliberate, controlled movement and preset withdrawal speed, as this is the coating thickness-determining step of the dip-coating technique [21].

2. Coating Characterisation Methods

Barrier coatings are typically analysed using physical, chemical, and electrochemical methods to gather essential information for comprehensive characterisation.

2.1. Physical Methods

Physical methods include wettability studies, adhesion and coating thickness assessments.

The wettability of a coating is an essential parameter, as it determines the rate of adherence or spreading of a liquid on the surface of the coating [22]. In order to obtain highly resistive anti-corrosion coatings, these need to present low wettability and, as such, high contact angle values. Contact angles are measured between the substrate-liquid interface of the droplet analysed. Such measurements are carried out in highly vapour-saturated atmospheres [23].

Another important parameter in the performance characterisation of barrier coatings is coating adhesion. This refers to the strength of the physical bond between the coatings and the metal surface to which these are applied. Adhesion is determined by the energy necessary to remove a coating. The degree of delamination is assessed by the standards in ASTMD3359, which also leads to accurate adhesion establishment [24].

The last of the addressed physical characterisation steps is coating thickness assessment. Coating thickness studies provide insight into how deeply corrosive media penetrate barrier coatings. The easiest techniques for its determination are by magnetic induction and Eddy current. The two are similar in methodology: a magnetic probe is placed on the coated metal substrate, measuring the strength of the magnetic field between the magnetic coil and the substrate. While magnetic iduction is suitable for ferrous materials, Eddy current allows for non-ferrous materials to be similarly assessed by generating their own opposing electromagnetic fields [25].

2.2. Microscopic and Spectroscopic Methods

Chemical analysis methods can be split into two distinct groups: microscopy and spectroscopy techniques.

Microscopy techniques provide insight into the structure and integrity of barrier coatings, enabling the determination of morphology, elemental analysis, and coating uniformity.

Transmission electron microscopy (TEM) was employed to analyze the internal structure of the solid barrier coating material using an accelerated, parallel electron beam that interacts with the atoms of the solid sample [26].

Scanning electron microscopy (SEM) was used to determine coating surface morphology and uniformity. Paired with energy-dispersive x-ray (EDS) spectroscopy, elemental composition of cross-sectioned samples can be determined. The technique focuses an electron beam through anode and condenser lenses onto a solid sample, interacting with its electrons [27].

Spectroscopy techniques offer insight into the chemical structure of the coatings and inhibitors as well as intramolecular inhibitor reactions, functional groups and adsorption mechanisms can be identified.

Fourier-transform infrared spectroscopy (FTIR), a technique reliant on the adsorption and transmission of infrared waves by the studied sample, is often used in corrosion studies to identify the composition of different corrosion products. It offers a deeper understanding of the protection mechanisms of barrier coatings by revealing specific bonding modes [28]. It is often considered to provide a molecular fingerprint of the studied samples.

Raman spectroscopy is used to identify the structural fingerprint of molecules, providing more information on the molecular structure and internal ordering of the studied samples. It serves a purpose similar to FTIR in corrosion studies. Raman is a more sensitive technique regarding non-polar symmetric bonds and vibrations and can be a suitable complementary tool to FTIR [29, 30].

UV-vis spectroscopy subjects the sample to a light beam within the visible and ultraviolet spectrums, and determines the amount of light absorbed by the sample at specific wavelengths. It is applied for both qualitative and quantitative analysis [31].

Electrochemical Methods

Electrochemical analysis methods are based on the measurement of the current or potential of an electrochemical cell. The study focuses mainly on potentiometric measurements.

Open circuit potential (OCP) represents the resting potential of an investigated system, commonly applied in corrosion studies. It is a non-invasive method that doesn’t involve any current flowing through the system [32]. The measurement provides the basis for the establishment of the thermodynamic stability of electrochemical reactions. It is measured in a three-electrode cell composed of a working electrode (WE), a reference electrode (RE) and a counter electrode (CE). OCP values vary in specific regions around the potential of the working electrode's material.

Electrochemical impedance spectroscopy (EIS) is a non-invasive electrochemical technique applied to determine mass-transfer, charge-transfer, and diffusion processes, while also providing information on the protection mechanism and kinetics of barrier coatings. It operates by the application of an alternating current in a range of frequencies, from high, where double layer capacitance occurs, to low, where slow processes such as charge transfer and diffusion can be brought to light [33]. It is also an effective tool for identifying failure points in barrier coatings.

Linear polarization is a technique used to determine the corrosion rate of a metallic substrate. By applying a small potential of 10 to 20 mV to the work electrode, the resulting current follows Ohm's law, making the relationship linear. The slope of the obtained curve results in the polarization resistance (Rp) value. The Stern-Geary [34] equation allows for further determination of corrosion rates. This technique allows for the in situ monitoring of the metal degradation process.

Potentiodynamic polarisation is based on the variation of the potential of the working electrode in relation to the reference electrode and the recording of the generated current. Potential variation applied in a ±200 mV interval around the OCP values generates oxidative/reductive reactions on the surface of the electrode. It is an invasive technique because of the high potential variation. Polarisation curves are the result of this process and are composed of cathodic and anodic branches. These, in the Tafel interpretation, give light to information on electrode kinetics, corrosion rate, inhibition efficiency and even reaction mechanisms [35].

II. Original Contribution

4. Anti-corrosive Polystyrene Coatings Modified with Tannic Acid on Zinc and Steel Substrates [36]

Corrosion is the gradual degradation of metals due to harsh environments, and researchers seek ways to prevent or reduce it. Anticorrosion methods include active protection via metal alloys and passive protection through barrier coatings. Due to health and environmental concerns, non-toxic, chromate-free organic and inorganic coatings are now preferred over older toxic technologies.

Polystyrene (PS), a vinyl polymer made from styrene, is widely used in plastic production and, due to its thermal properties, in making Styrofoam. In corrosion protection, PS has been used in copolymers or as microcapsules containing corrosion inhibitors. Its protective performance can be enhanced by incorporating inhibitors like rare earth salts (e.g., $CeCl_3$), organic compounds (e.g., benzotriazole), and gallotannins (e.g., tannic acid), which form protective complexes on metal surfaces.

Due to their controlled release capabilities, nanocontainers are effective carriers for corrosion inhibitors in self-healing coatings. Examples include urea-formaldehyde microcapsules and mesoporous silica nanoparticles loaded with inhibitors like molybdate or benzotriazole, often sealed with tannic acid.

This study investigates the effectiveness of PS coatings on zinc and steel, with and without tannic acid, using two methods: (i) direct addition of tannic acid before polymerization, and (ii) use of silica nanocontainers impregnated with tannic acid. Coatings were applied by dip-coating and analyzed through electrochemical impedance spectroscopy (EIS), transmission electron microscopy (TEM), adhesion, and thickness measurements.

Transmission electron microscopy (TEM) analysis confirmed that the synthesized mesoporous silica nanocontainers had diameters ranging from 20 to 50 nanometers, which is sufficient to accommodate tannic acid molecules, given their approximate size of 1.85 × 1.65 × 1.01 nm. This supported the suitability of the nanocontainers for carrying the corrosion inhibitor. *(Figure 4.2)*

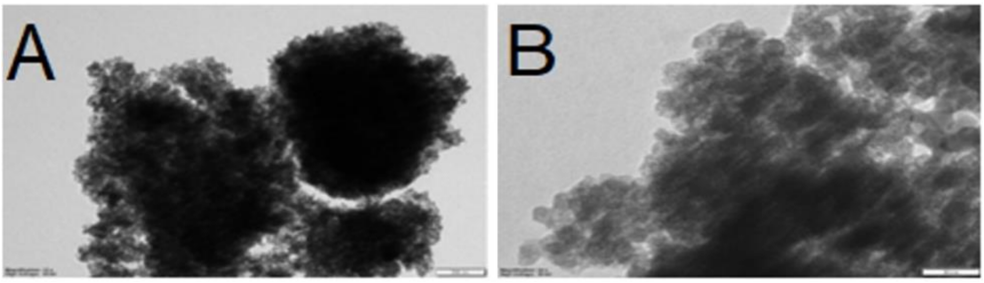

Figure 4.2. Transmission electron microscopy images reflecting a cluster of synthesised mesoporous silica nanocontainers at scales of **A.** 200 nm respectively **B.** 50 nm

Adhesion tests revealed that the incorporation of tannic acid slightly reduced the adherence of the coatings on both zinc and mild steel. This effect may be due to the rapid formation of metal-tannate complexes before polystyrene polymerisation, leading to the development of an intermediate porous layer that weakens overall adhesion. Mild steel substrates consistently exhibited lower adhesion than zinc, likely due to their higher reactivity and rougher surface condition after pretreatment. Thickness measurements showed that the addition of nanocontainers or tannic acid increased the coating thickness to approximately 20 μm in all modified samples. *(Table 4.1)*

Table 4.1. Results of adhesion and layer thickness evaluation for the PS, PS + NC, PS + TA and PS + TA + NC coatings on zinc and mild steel substrates

Sample	**Layer thickness (μm)**	**Adhesion (%)**	**Adhesion Class (ASTM)**
Zn / PS	8.0	95	4B
Zn / PS + N C	20.0	95	4B
Zn / PS + TA	21.8	91	3B
Zn / PS + TA + NC	21.8	87	3B
Mild steel / PS	8.0	~85	2B
Mild steel / PS + NC	20.0	~ 65	1B
Mild steel / PS + TA	21.8	~85	2B
Mild steel / PS + TA + NC	21.8	~85	2B

Wettability measurements indicated a slight increase in hydrophilicity when tannic acid or silica nanocontainers were introduced into the coating matrix. This was expected due to the polar nature of both additives, although the overall decrease in contact angle was not significant. *(Figure 4.3)*

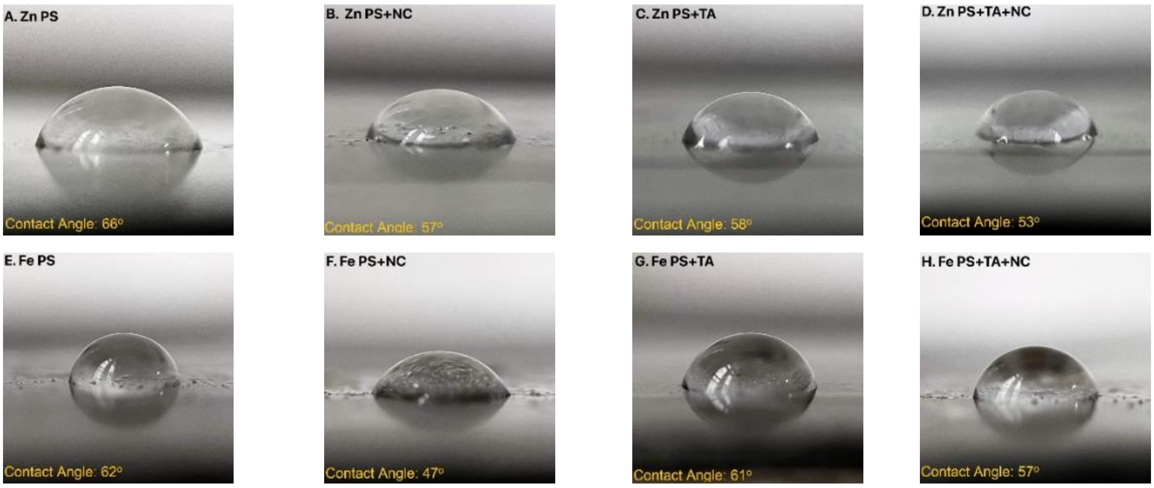

Figure 4.3. Wettability measurements (at 0 min) effectuated with 20 µL droplet of 0.2 g / L Na2SO4 electrolyte solution on the following coatings: **A.** Zn PS, **B.** Zn PS + NC, **C.** Zn PS + TA, **D.** Zn PS + TA + NC, **E.** Fe PS, **F.** Fe PS + NC, **G.** Fe PS + TA, **H.** Fe PS + TA + NC

Electrochemical impedance spectroscopy (EIS) showed that the undoped polystyrene coating improved impedance relative to bare zinc, while the addition of empty nanocontainers (PS + NC) decreased impedance, suggesting that they act as defects within the coating and compromise its protective ability. However, when tannic acid was introduced—either directly into the polystyrene matrix or through impregnated nanocontainers—corrosion resistance improved significantly. The direct addition of tannic acid (PS + TA) resulted in higher impedance values than the nanocontainer approach (PS + TA + NC), likely due to better compatibility and retention of the tannic acid in the polymer matrix. On mild steel, similar trends were observed: tannic acid enhanced corrosion resistance in both forms, though to a lesser extent than on zinc. This reduced effectiveness may be attributed to the mild steel's rapid oxidation and lower compatibility with passive coatings. Overall, tannic acid was confirmed to be an effective anticorrosive agent, with superior performance when directly incorporated into the polystyrene coating. *(Figures 4.4. and 4.5.)*

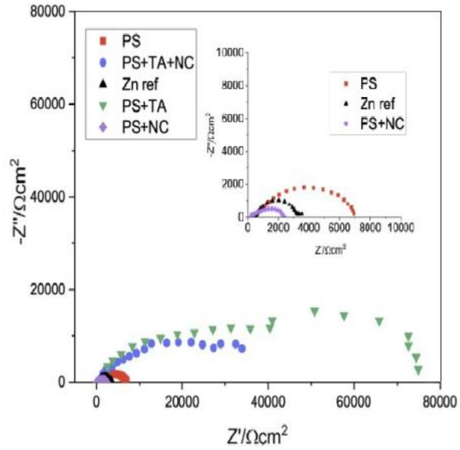

Figure 4.4. EIS plots of the Zn ref, PS, PS + NC, PS + TA, PS + TA + NC coatings on Zn substrates in 0.2 g/L Na_2SO_4 solution (pH = 5)

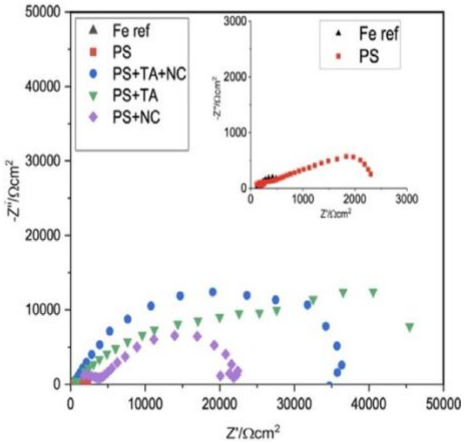

Figure 4.5. EIS plots of the Fe ref, PS, PS + NC, PS + TA, PS + TA + NC coatings on mild steel substrates in 0.2 g/L Na_2SO_4 solution (pH = 5)

5. Electrochemical Investigation of the Corrosion Inhibiting Effect of Organic Paints Doped with Benzotriazole Coated on Steel Substrates [37]

Organic coatings, such as primers and undercoating paints, remain one of the most widely used strategies for this purpose, often enhanced with corrosion inhibitors or hydrophobizing agents to improve their performance. The incorporation of inhibitors like benzotriazole (BTA) into the coating matrix has been shown to increase corrosion resistance and, in some cases, confer self-healing properties.

This study evaluates the electrochemical behavior of mild steel coated with two commercial paint systems: an alkyd primer (Grund) and a rubberized undercoating paint (Autovapant), both used with and without BTA addition. The coatings were applied via dip-coating, and in certain samples, a pretreatment layer containing gallic acid, barium sulfate, and monoethylene glycol was applied prior to coating. The goal was to determine whether these accessible, low-complexity modifications—BTA incorporation and pretreatment—could enhance the anti-corrosion and self-repairing properties of the paints, even after mechanical damage.

Electrochemical characterisation using potentiodynamic polarisation revealed significant reductions in corrosion current densities when BTA was incorporated into the coatings. The primer doped with BTA showed the greatest improvement, with a corrosion current density decrease of over 300-fold compared to uncoated steel and an inhibition efficiency exceeding 99% (*Figure 5.1*). While the undercoating paint also benefited from BTA addition, the effect was less pronounced, likely due to its higher porosity. Electrochemical impedance spectroscopy was also applies to further study coating behaviour. Pseudo-porosity calculations confirmed this difference, indicating greater electrolyte permeability through the undercoating paint, which correlates with the observed reduction in protective performance.

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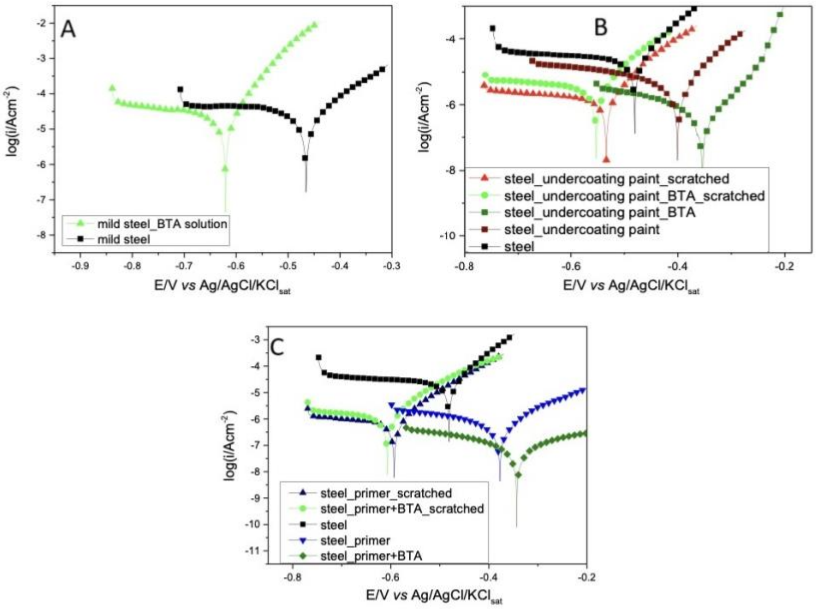

Figure 5.1. Potentiodynamic polarization curves for painted and artificially damaged painted mild steel exposed to accelerated conventional corrosion tests in the absence and in the presence of BTA

Upon scratching the coated samples to simulate physical damage, the presence of BTA remained beneficial. Although corrosion current densities increased compared to intact coatings, the doped layers still exhibited a notable self-healing tendency, particularly in the primer-based systems. The data suggested that BTA, when embedded in the matrix, is capable of migrating to exposed areas, forming passivating complexes and slowing corrosion processes. This self-healing behaviour was further supported by electrochemical impedance spectroscopy (EIS), which provided detailed insight into the underlying protection mechanisms.

EIS measurements demonstrated that BTA-containing coatings possessed higher charge transfer resistance and improved impedance behavior compared to undoped samples. These effects were especially prominent in the primer-based coatings. Fitted Nyquist plots and equivalent electrical circuits confirmed that BTA significantly increased the resistance to electrolyte infiltration, charge transfer, and lateral diffusion of corrosive species (*Figure 5.3.*). Additionally, breakpoint frequency analysis revealed a shift toward a more capacitive behavior, particularly in the primer + BTA systems, suggesting improved barrier performance and slower water uptake.

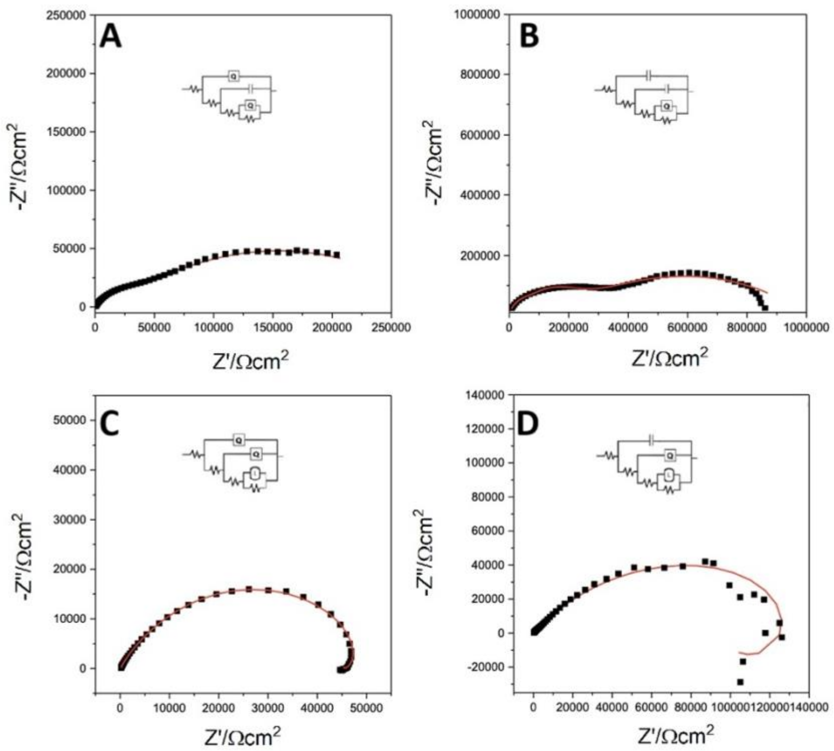

Figure 5.3. Experimental (scattered symbols) and simulated (continuous lines) Nyquist impedance spectra for steel/primer and steel/undercoating paint samples in the absence (**a**,**c**) and in the presence (**b**,**d**) of BTA and their corresponding electrical equivalent circuits (insets)

Pretreatment prior to coating application further enhanced corrosion resistance, as observed in both polarization and EIS data. Coating thickness increased slightly in pretreated samples, and the adhesion class of the undercoating paint improved to the maximum rating (5B). Over time, pretreated samples retained higher impedance values, even under immersion and mechanical damage. BTA-containing, pretreated coatings—particularly those using the primer—displayed the most stable protection throughout the testing period. This synergistic effect was most apparent in long-term EIS measurements, where pretreatment delayed degradation and helped maintain high coating resistance (*Figure 5.5.* and *Figure 5.6.*).

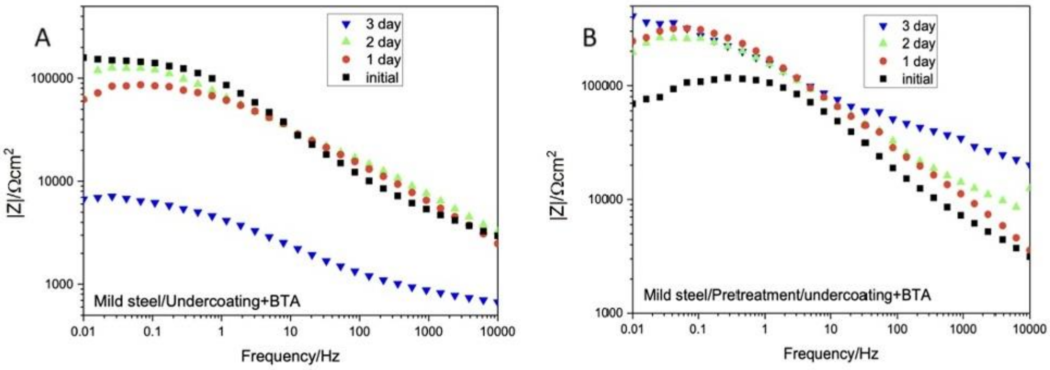

Figure 5.5. Time evolution of EIS diagrams of mild steel/undercoating + BTA (**a**) and mild steel/pretreatment/undercoating + BTA (**b**) soaked in 3% NaCl.

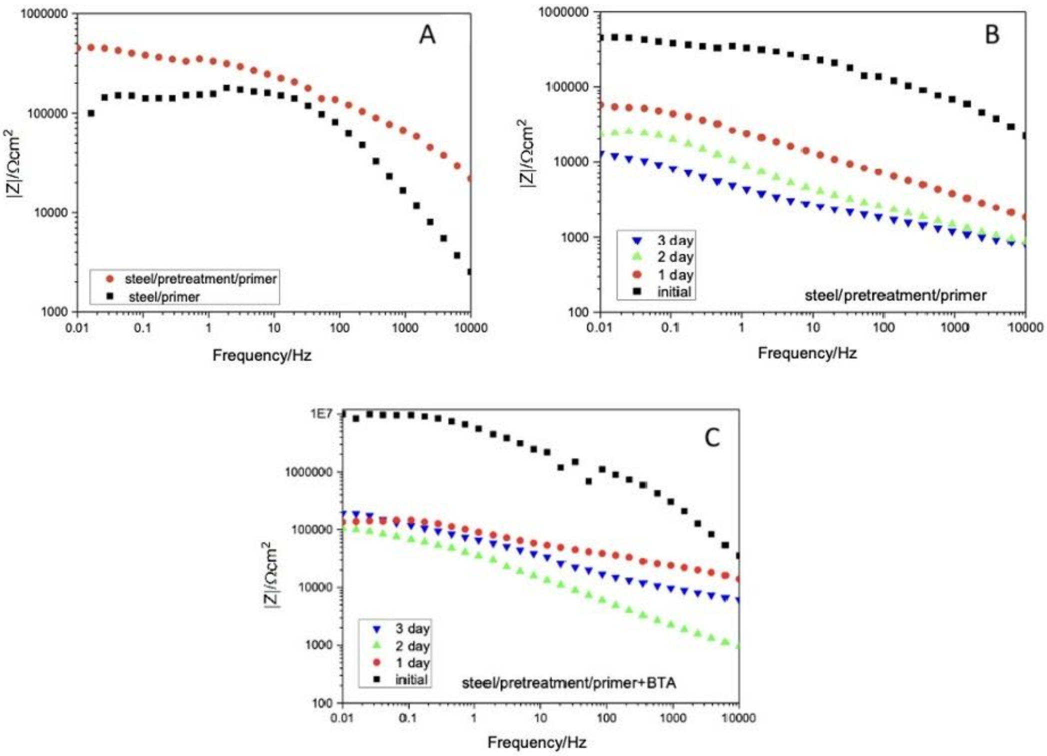

Figure 5.6. Bode diagrams for steel/primer and steel/pretreatment/primer (**A**); the time evolution of steel/pretreatment/primer (**B**) and steel/pretreatment/primer + BTA (**C**) samples.

The adhesion of the coatings, tested by the lattice notch method, confirmed that the undercoating paint adhered better to the substrate than the primer, though both systems achieved adequate mechanical performance. In terms of coating integrity, the undercoating paint presented excellent adhesion (Class 5B), while the primer reached Class 4 B. The improved performance in the primer + BTA + pretreatment samples, despite their slightly lower adhesion, highlights the importance of chemical composition and porosity in determining electrochemical protection efficiency.

Overall, this study demonstrates that easily applicable commercial paint systems can be significantly improved through the incorporation of BTA and a simple surface pretreatment. The primer system, in particular, proved to be an effective matrix for inhibitor embedding, showing superior corrosion resistance and a more pronounced self-healing response. These enhancements suggest that smart-like functionalities can be achieved without complex formulations or nanotechnology-based delivery systems. The combination of BTA and pretreatment thus offers a practical, cost-efficient solution for corrosion protection of steel components exposed to aggressive environments.

6. Influence of Embedded Inhibitors on the Corrosion Resistance of Zinc Coated with Mesoporous Silica Layers [38]

This study explores the corrosion resistance and permeability of mesoporous silica sol–gel coatings deposited on zinc substrates, with special focus on their potential self-healing behavior. Two different templating agents were employed—CTAB, a cationic surfactant, and Pluronic PE 10,300, a non-ionic block copolymer—to generate mesoporosity. The coatings were further impregnated with corrosion inhibitors (1H-benzotriazole and CTAB) and tested in sodium sulfate solutions (pH 5) to assess their protective performance.

The self-healing mechanism is based on the entrapment and gradual release of corrosion inhibitors from within the porous structure when the coating is damaged. CTAB served a dual role, functioning both as a templating agent and as an inhibitor, due to its ability to remain adsorbed within silica pores. BTA, a well-known inhibitor for copper and steel, was also tested for its affinity to accumulate within the silica matrix.

Electrochemical characterization was conducted using open circuit potential (OCP), Tafel polarization, and Electrochemical Impedance Spectroscopy (EIS). The most significant corrosion protection was observed in hydrophobic samples that had been loaded with BTA and subsequently silylated, particularly those templated with Pluronic (*Figure 6.2.*). These coatings exhibited inhibition efficiencies above 90% and substantially lower corrosion current densities (Table 2.1), indicating strong barrier properties and effective inhibitor retention.

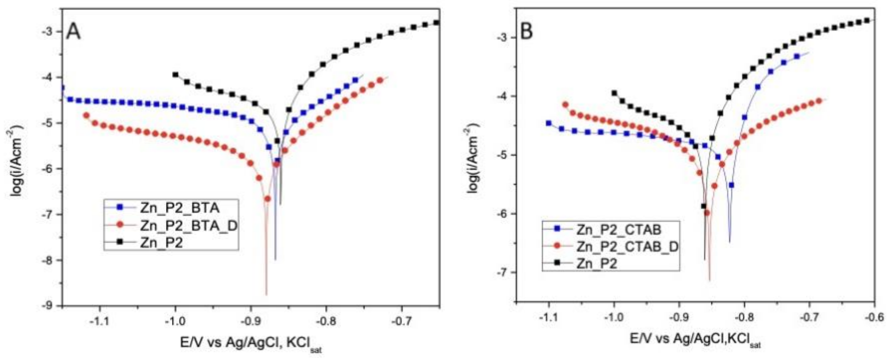

Figure 6.2. Potentiodynamic polarization curves recorded on Zn wafers coated with Pluronic templated porous silica coating (P2), impregnated with BTA (P2_BTA) and CTAB (P2_CTAB) without and with hydrophobization with dimethyldichlorosilane (P2_BTA_D and P2_CTAB_D). Experimental conditions: scan rate, 10 mV/min.

While BTA demonstrated better performance in solution-phase tests, CTAB showed more effective incorporation into the porous silica matrix. Nonetheless, the combination of BTA loading and surface hydrophobization offered the best corrosion resistance in coated zinc substrates. The beneficial effect of hydrophobization was further confirmed by EIS measurements, which revealed enhanced impedance values for silylated coatings (*Figure 6.5.*).

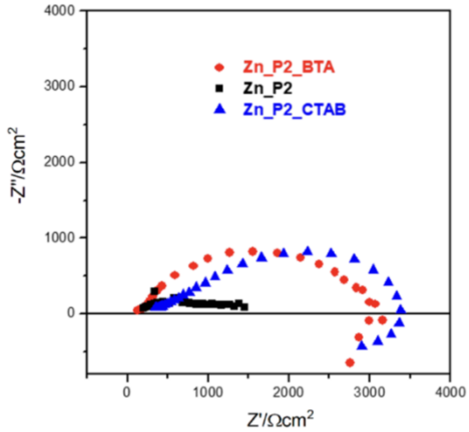

Figure 6.5. The Nyquist diagrams of Zn wafers coated with Pluronic templated porous silica coating (P2), impregnated with BTA (P2_BTA) and CTAB (P2_CTAB)

Overall, the results highlight that hydrophobization is a critical final step in the preparation of mesoporous silica coatings. When paired with suitable corrosion inhibitors, particularly BTA, it leads to significantly improved long-term protection of zinc substrates.

7. Tannic Acid Reinforced Sol-gel Silica Coatings for Corrosion Protection of Zinc Substrates [39]

The study explores the corrosion protection performance of compact silica coatings enhanced with tannic acid (TA), developed via the sol-gel method and applied through dip-coating on zinc substrates. The research is set in the broader context of replacing toxic chromate-based coatings with environmentally friendly alternatives, highlighting the promise of nanotechnology-based protective layers. Silica, known for its strong metal adhesion due to M-O-Si bonds, was selected as the base material. The innovation lies in integrating TA into the silica network during the sol stage to achieve chemical interactions and network reinforcement before gelation.

Tannic acid, a natural, non-toxic corrosion inhibitor, was selected for its ability to form metal-tannate complexes and its known protective effects on various metals. However, while its action in solution is well-documented, this study uniquely focuses on its incorporation into a solid silica matrix on zinc — a less explored yet highly relevant substrate.

The SiO_2 sols were synthesized using TEOS, ethanol, and HCl under controlled conditions. TA was introduced via a two-stage process that allowed sufficient interaction between hydrolyzed TEOS and TA before full silica network formation. Coatings with varying TA concentrations (0.5 wt%, 1 wt%, and 2 wt%) were prepared and thermally cured at 150 °C. Only the 1 wt% TA composition yielded optimal adhesion and structural integrity, as 2 wt% caused cracking and 0.5 wt% provided negligible improvement.

Electrochemical Impedance Spectroscopy (EIS) over a 28-day wet-dry cycle revealed that pure SiO_2 coatings stabilize after 21 days due to the slow polycondensation process, which was essential for ensuring consistent measurements. Among all tested systems, the Zn/(SiO_2 + 1 wt% TA) coating showed the highest impedance values and superior capacitive response, attributed to the dual effect of TA as both a reinforcing agent and inhibitor. The best-performing coating system also exhibited the lowest pseudo-porosity, implying a dense, compact structure less permeable to corrosive agents (*Figure 7.2.*).

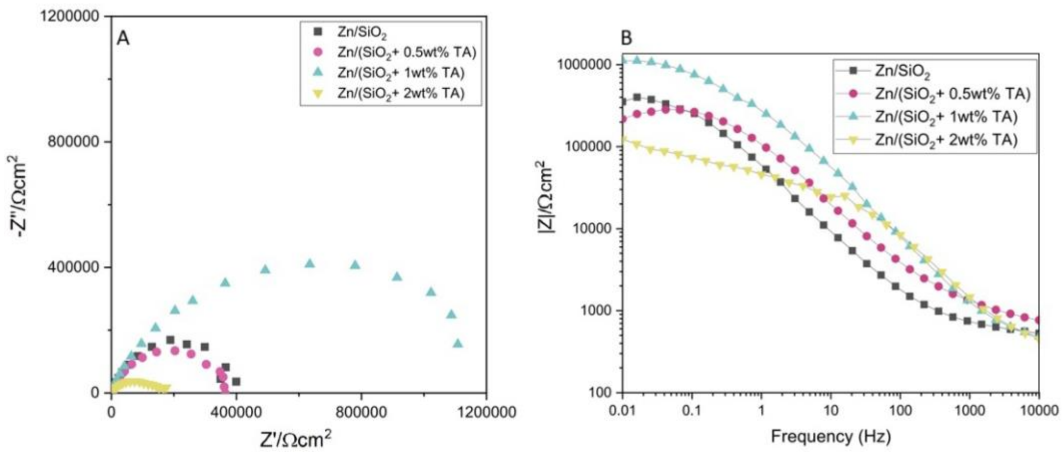

Figure 7.2. **A**. Nyquist and **B**. Bode diagrams of Zn/SiO_2 vs. Zn/(SiO_2 + 0.5 wt% TA), Zn/(SiO_2 + 1 wt% TA) and Zn/(SiO_2 + 2 wt% TA) coatings

Potentiodynamic polarization curves further confirmed the outstanding inhibition efficiency of the 1 wt% TA-modified SiO_2 coatings, which reduced corrosion current by more than an order of magnitude compared to uncoated zinc and outperformed both the pure SiO_2 and 0.5 and 2 wt% TA systems.

Morphological and structural characterization supported the electrochemical findings. FT-IR and Raman spectroscopy indicated the presence of Si–C and Si–O–C bonds in the 1 wt% TA system, revealing successful chemical integration of TA into the silica network. Raman spectra (*Figure 7.7.*) exhibited specific peaks associated with Si–C/Si–O–C, strengthening the claim of a reinforced hybrid matrix.

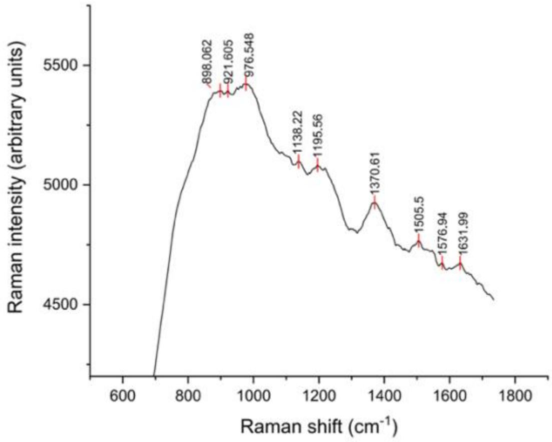

Figure 7.7. Raman spectroscopy measurements performed on SiO_2 + 1 wt% TA precipitates powder from the tannin containing SiO_2 sol.

Wettability studies using the sessile drop method showed that Zn/(SiO_2 + 1 wt% TA) coatings had higher contact angles and a slower decline in wettability over time compared to pure SiO_2, suggesting reduced hydrophilicity, which correlates with improved corrosion resistance.

SEM analysis confirmed the long-term integrity of the coatings. After 60 days of immersion and post-polarisation measurements, both Zn/SiO_2 and Zn/(SiO_2 + 1 wt% TA) retained their morphology, with no visible signs of degradation or delamination. In particular, the 1 wt% TA coating preserved a uniform surface, highlighting its resistance to aqueous corrosion.

In conclusion, the Zn/(SiO_2 + 1 wt% TA) coating demonstrates significant potential as an eco-friendly, efficient corrosion protection system for zinc substrates. Its ability to combine high adhesion, low porosity, and chemically reinforced structure positions it as a strong candidate for replacing conventional coatings in industrial applications.

8. Effect of the Preparation Method on the Properties of Eugenol-Doped Titanium Dioxide (TiO_2) Sol-Gel Coating on Titanium (Ti) Substrates [40]

This research focuses on the development of eugenol-functionalized TiO_2 coatings for titanium-based biomedical implants, using the sol–gel method. The coatings were engineered to improve both corrosion resistance and antibacterial performance, two critical properties that influence the long-term success of implants, particularly in preventing post-surgical complications and biofilm formation.

Titanium and its alloys, especially Ti6Al4V (Grade 5), are widely used in orthopedics and dentistry due to their mechanical strength, corrosion resistance, and biocompatibility. Despite these advantages, titanium implants are prone to bacterial colonization and exhibit limited long-term protection against localized corrosion. Although a native TiO_2 layer forms spontaneously on the surface, it lacks the robustness required for long-term stability under physiological conditions.

To address these limitations, the study explored the sol–gel synthesis of TiO_2 coatings modified with eugenol, the principal component of clove oil, which possesses well-documented antimicrobial, antioxidant, and anti-inflammatory properties. Eugenol has previously demonstrated corrosion-inhibiting behavior on various metallic surfaces and is widely accepted in dental and medical applications.

Two different eugenol incorporation strategies were employed:

Post-deposition impregnation of pre-formed TiO_2 layers with ethanol-based eugenol solutions (denoted as TiO_2/Eug), and

Direct addition of eugenol into the sol prior to deposition (denoted as Eug–TiO_2). To preserve the functional properties of eugenol, coatings were heat-treated at a relatively low temperature of 150 °C.

Coatings were applied *via* dip-coating onto Ti6Al4V alloy (TiGr5), commercially pure titanium (cp-Ti), and glass substrates, followed by thermal stabilisation. Four types of samples were analyzed: unmodified TiO_2, TiO_2/Eug (impregnated), Eug–TiO_2 (directly loaded), and control samples for comparison.

The electrochemical behaviour of the coatings was evaluated using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarisation (PDP) in Hank's physiological solution. The results clearly indicated that both eugenol-modified systems exhibited enhanced corrosion resistance compared to pure TiO_2 coatings. Notably, Eug–TiO_2 samples demonstrated the highest impedance values and lowest corrosion current densities, confirming superior barrier properties (*Figure 8.3. and Figure 8.5.*). The enhancement was particularly pronounced at lower eugenol concentrations (10^{-2} M), which appeared optimal for preserving the coating structure without compromising performance.

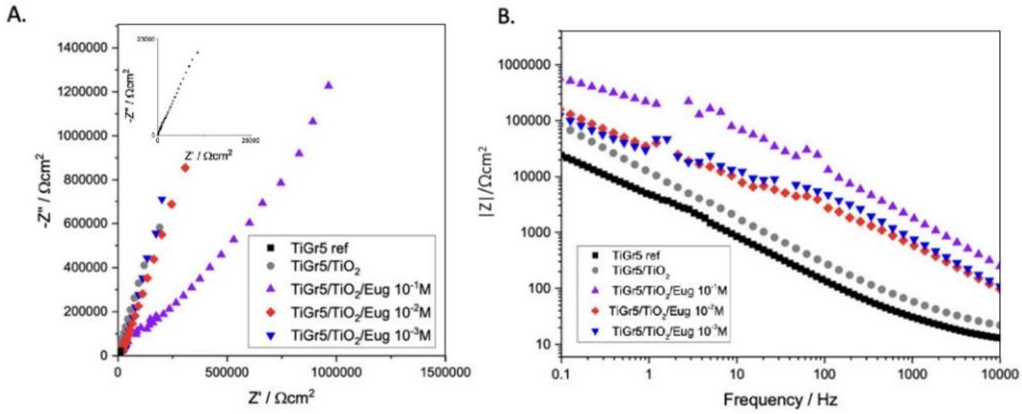

Figure 8.3. Nyquist (**A**) and Bode magnitude (**B**) EIS spectra of TiGr5 reference, TiGr5 coated with undoped TiO2, and with Eug impregnated coatings, TiO2/Eug 10^{-1} M, TiO2/Eug 10^{-2} M and TiO2/Eug 10^{-3} M.

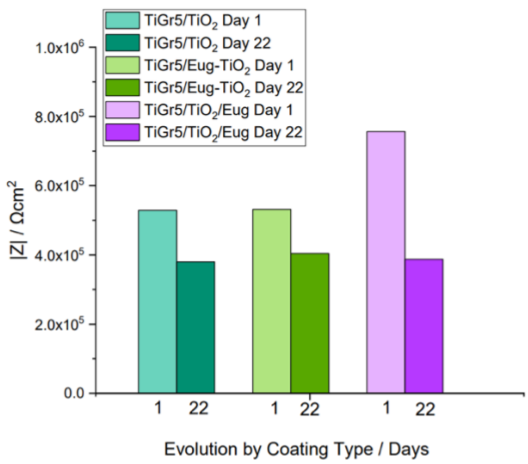

Figure 8.5. Histogram depicting the impedance modulus values of TiO_2, Eug–TiO_2, and TiO_2/Eug on Day 1 and Day 22 of the long-term evaluation.

The antibacterial properties of the coatings were tested against *Escherichia coli* using a standard EUCAST-based microbiological protocol. All eugenol-containing samples inhibited bacterial growth, but Eug–TiO_2 coatings consistently showed the greatest antimicrobial effect, even after prolonged incubation periods (Figure 8.11.). These findings confirm that the direct incorporation of eugenol into the sol matrix facilitates more uniform distribution and sustained bioactivity, offering an effective strategy for bacterial inhibition.

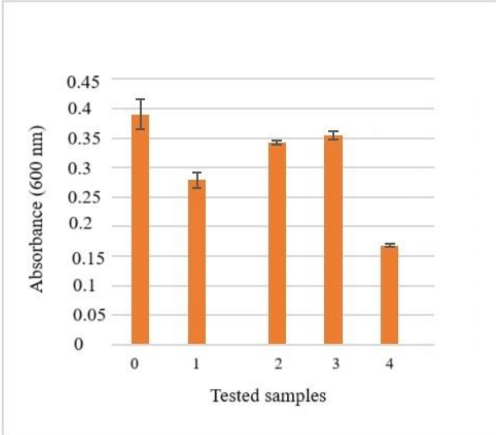

Figure 8.11. Antimicrobial analysis results for 0. blank sample, 1. TiO_2, 2–3. TiO_2/Eug in the following concentrations 10^{-1} M, 10^{-2} M, and 4. Eug-TiO_2.

Adhesion strength was assessed using a standardized cross-cut tape test, in which all coating types achieved high mechanical stability, with minimal detachment and good substrate cohesion. The coating thickness, measured via magnetic induction using a TROTEC BB25 gauge, was consistent across all samples, providing reproducible coverage within the desired biomedical range.

Chemical characterisation using FT-IR spectroscopy confirmed the successful retention of eugenol within the TiO_2 matrix, with specific absorption peaks corresponding to aromatic and phenolic groups. Raman spectroscopy further revealed the presence of Ti–O–C bonds in Eug–TiO_2 samples, supporting the hypothesis of chemical bonding between the eugenol and the sol–gel-derived TiO_2 network (Figure 8.7.). While some of the eugenol signals overlapped with dominant Ti–O–Ti vibrations, the key functional groups remained detectable.

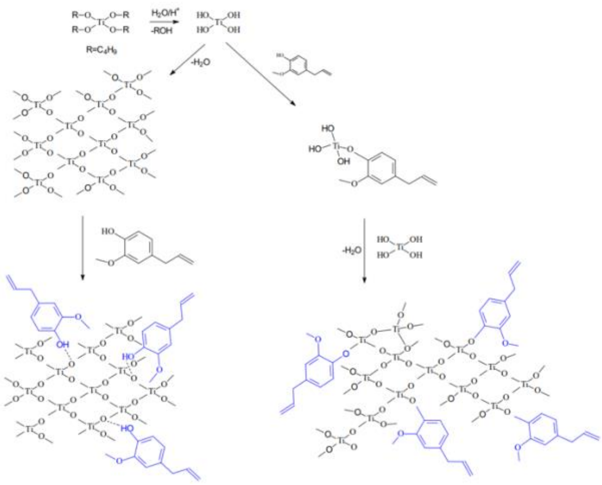

Figure 8.7. Scheme of the possible incorporation path of Eugenol into the TiO_2 matrix.

Surface morphology, analysed via SEM, demonstrated that all coatings were homogeneous, compact, and free of cracks. Importantly, eugenol-modified coatings exhibited a smoother and more uniform surface, likely contributing to their improved electrochemical and antibacterial behaviour. No significant differences in surface coverage were observed between TiGr5 and cp-Ti substrates, indicating good compatibility of the sol–gel process with both material types.

In summary, the sol–gel derived TiO_2 coatings modified with eugenol present a promising multifunctional platform for medical implant surfaces. The study demonstrates that incorporating eugenol directly into the sol not only improves corrosion resistance and bacterial inhibition but also maintains the coating's mechanical and structural integrity. These coatings represent a cost-effective and scalable solution for enhancing implant performance, with clear benefits for long-term patient safety and reduced risk of post-operative infection.

9. Silver Linings: Electrochemical Characterisation of TiO_2 Sol–Gel Coating on Ti6Al4V with $AgNO_3$ for Antibacterial Excellence [41]

The study focuses on the development of multifunctional TiO_2-based sol-gel coatings applied to Ti6Al4V (TiGr5) alloy substrates. These coatings were designed to provide both corrosion resistance and antibacterial properties for potential biomedical applications. Silver nitrate ($AgNO_3$) was incorporated using two distinct methods: (1) direct doping into the precursor sol (Ag-TiO_2) and (2) post-deposition impregnation into pre-formed TiO_2 films ($TiO_2/AgNO_3$). The goal was to retain silver in its ionic form to enable controlled biological release.

Electrochemical characterisation, which included electrochemical impedance spectroscopy and potentiodynamic polarisation, showed that the impregnated coatings ($TiO_2/AgNO_3$) at a concentration of 10^{-2} M exhibited the most favourable performance. Over a 22-day immersion period in a simulated physiological medium, these coatings maintained higher impedance values and lower corrosion current densities (*Figure 9.2.*). Additionally, the method of silver incorporation was found to significantly affect both the corrosion protection mechanism and the long-term stability of the film.

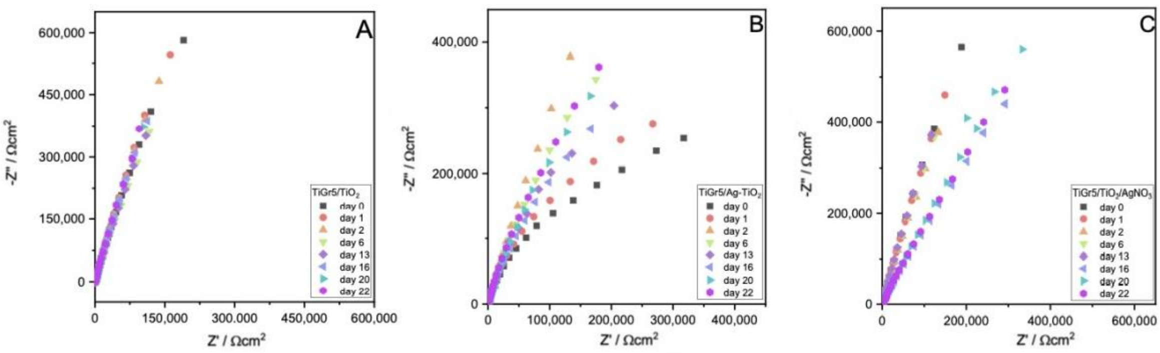

Figure 9.2.: Comparative Nyquist diagram for long-term study of **A.** TiGr5/TiO_2, **B**. TiGr5/Ag-TiO_2 and **C.** TiGr5/TiO_2/$AgNO_3$ with $AgNO_3$ present in both enhanced systems in a concentration of 10^{-2} M

Antibacterial tests against *E.coli* revealed that all silver-containing coatings significantly reduced bacterial growth. Impregnated films exhibited superior short-term antibacterial action due to faster ion release, while doped coatings (Ag-TiO_2) provided more gradual and sustained antimicrobial effects, beneficial for long-term applications (*Figure 9.6.*).

Additional characterisation confirmed that impregnated coatings resulted in increased film thickness due to $AgNO_3$ surface adsorption, while all coatings achieved strong adhesion to the substrate (ASTM D3359, 4B classification).

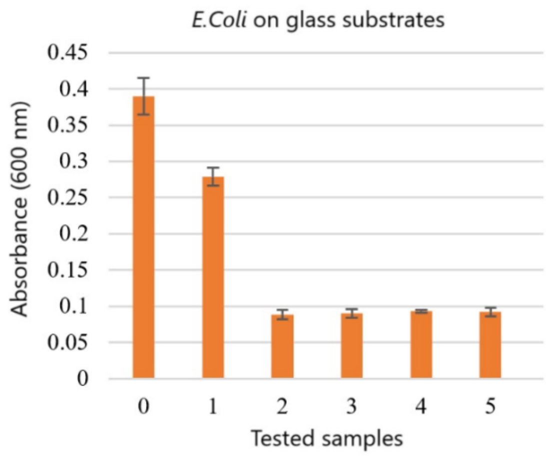

Figure 9.6. Antimicrobial analysis performed on **0.** Untreated sample in bacterial suspension and medium, **1**. TiO_2 coating **2–4**. TiO_2/$AgNO_3$ (10^{-3} M, 10^{-2} M, 10^{-1} M), **5.** TiGr5/Ag-TiO_2

In conclusion, the $TiO_2/AgNO_3$ system created through post-deposition impregnation with 10^{-2} M $AgNO_3$ provides optimal corrosion resistance and antibacterial performance. These results position this system as a promising candidate for future biomedical coating applications.

General Conclusions

The present doctoral thesis provides a multidisciplinary and application-oriented contribution to developing corrosion-inhibiting and biofunctional coatings on metallic substrates. The research focuses on improving substrates with increasing relevance in biomedical and industrial applications—specifically zinc, carbon steel, and titanium alloys. It investigates various coating matrices, including organic-inorganic hybrids, pure sol-gel systems, and organic dispersions.

One of the main objectives of this work is to bridge the gap between academic novelty and practical applicability by incorporating natural and industrially relevant inhibitors into protective films. The originality of the thesis lies in its systematic comparison of doping and impregnation strategies, the preparation of novel coating systems using various methods, and the design of multifunctional surfaces that combine corrosion protection with additional properties, such as hydrophobicity and antibacterial activity.

In the study titled "Anti-corrosive Polystyrene Coatings Modified with Tannic Acid on Zinc and Steel," the main innovation is the demonstration that directly doping tannic acid during the solution preparation stage significantly enhances corrosion resistance. This method surpasses the corrosion resistance achieved through nanocontainer-mediated incorporation.

The publication "Electrochemical Investigation of the Corrosion Inhibiting Effect of Organic Paints Doped with Benzotriazole Coated on Steel Substrates" introduces the concept that a widely used inhibitor, namely benzotriazole (BTA), can be effectively integrated into industrially available primer and undercoat systems to induce both corrosion protection and short-term self-healing. This study provides compelling evidence that functional additives can be integrated into off-the-shelf coating systems, thereby extending their utility and demonstrating the untapped potential of existing formulations for smart protection.

The third study, entitled “Influence of Embedded Inhibitors on the Corrosion Resistance of Zinc Coated with Mesoporous Silica Layers”, proves that even small quantities of benzotriazole, when incorporated into porous sol–gel silica coatings, remain chemically active and electrochemically effective. This contradicts the commonly held view that high inhibitor loading is required for corrosion mitigation. Instead, the study reveals that localised interaction at defect sites enables substantial corrosion protection.

The fourth study, entitled “Tannic Acid-Reinforced Sol-Gel Silica Coatings for Corrosion Protection of Zinc Substrates”, presents a significant advancement in the chemical reinforcement of the silica network by incorporating low concentrations of tannic acid. Spectroscopic, electrochemical, and physicochemical analyses confirm that tannic acid not only improves the compactness and durability of the coatings but also enhances their hydrophobicity and morphological stability. This research offers a new, environmentally friendly strategy for improving the barrier properties of sol-gel films through molecular-level engineering.

The fifth article, entitled “Effect of the Preparation Method on the Properties of Eugenol-Doped Titanium Dioxide (TiO2) Sol-Gel Coating on Titanium (Ti) Substrates”, presents an original approach for the introduction of the natural compound, eugenol, into the titanium dioxide polymer matrix. The novelty of this study lies in enhancing both anticorrosive and antimicrobial properties through a single additive, facilitated by the formation of Ti–O–C bonds. The obtained coating showed superior impedance values and measurable E. coli inhibition, signifying its relevance for the development of antibacterial surfaces on titanium-based medical implants.

The last article, named “Silver Linings: Electrochemical Characterisation of TiO_2 Sol–Gel Coating on Ti6Al4V with $AgNO_3$ for Antibacterial Excellence”, compares the electrochemical and antibacterial performance of TiO_2 coatings modified via doping vs. via impregnation with silver nitrate. The innovation of this work stems from identifying the distinct roles of these incorporation strategies: while impregnated coatings yield superior short-term corrosion resistance and antibacterial efficacy, doped variants provide longer-lasting antimicrobial effects. This insight enriches the framework for silver-modified coatings, particularly for biomedical applications where both immediate and sustained antibacterial action may be required.

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