

## Optimizing copper anticorrosive protection: properties of GPTMS-TiO<sub>2</sub> hybrid organic-inorganic sol-gel coatings via the dip-coating technique

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### ABSTRACT

This paper reports a novel coating containing activated TiO<sub>2</sub> for improving corrosion resistance of Cu. In this study, three types of coatings were compared: one made from GPTMS (3-Glycidopropyltrimethoxysilane) (GC1), and two hybrid sol-gel coatings derived from G1 (solution organic) and activated with titanium. The Class I (GC2) coatings contained crystallized TiO<sub>2</sub> particles integrated into the matrix, while the Class II (GC3) coatings used the liquid precursor TTIP (titanium (IV) isopropoxide). The three coatings, with thicknesses of  $0.777 \pm 0.5 \mu\text{m}$  (GC1),  $2.054 \pm 0.5 \mu\text{m}$  (GC2), and  $3.774 \pm 0.23 \mu\text{m}$  (GC3), were analyzed using XRD, optical profilometry, and SEM techniques. GC1 and GC3 exhibited uniform structures, while GC2 showed cracks due to TiO<sub>2</sub> particles. After salt spray exposure per ASTM B117, the coatings were labeled GCE1, GCE2, and GCE3 for evaluation. Salt spray exposure caused SiO<sub>2</sub> precipitates, impacting coating performance. GC3, with TTIP, showed a uniform surface and controlled roughness, leading to superior corrosion resistance (95% efficiency, 2764  $\Omega$ ), outperforming GC2 (94% efficiency, 1331  $\Omega$ ) and the substrate (918  $\Omega$ ). TTIP improved adhesion and barrier formation, while TiO<sub>2</sub> coatings (GC1, GC2) had increased roughness due to particle irregularities. GC3's thicker, well-integrated structure contributed to its enhanced performance in corrosive environments.

**Keywords:** 3glycidoxypropyltrimethoxysilane; Hybrid sol-gel coatings; Copper protection; Salt-spray test; Titanium (IV) isopropoxide.

### 1. INTRODUCTION

Copper and its alloys have several areas of application due to their high electrical conductivity, thermal conductivity, and malleability. They are crucial to the production of wires, copper sheets, pipes, electrical conductors, water service pipelines, industrial circuits, heat exchangers, and ship hull coatings [1–3]. In marine environments, however, exposure to corrosive weather conditions can lead to corrosion, causing material and economic losses [4]. For this reason, the corrosion of copper and its alloys in marine environments has been a research area of significant interest, studied through field tests and laboratory experiments [5, 6]. To protect surfaces of copper and alloys of other metals, sol-gel coatings based on silanes, produced with techniques such as electrochemical deposition and dip-coating, have been investigated [7–10]. These coatings function as effective barriers against corrosion, forming dense, crack-free micro-metric films due to the formation of -Si-O-Si- bonds during the condensation of silanol groups [11, 12]. Common formulations include silicon alkoxides and organic blends such as 3-glycidoxypropyltrimethoxysilane (GPTMS) [10, 13], tetraethylorthosilicate (TEOS) [10, 14], and methyltriethoxysilane (MTES) [15]. Silane-based sol-gel coatings stand out for their barrier effect, their ability to incorporate inhibitors, their adherence to various metal substrates, and their compatibility with added finishes. In their production, the effectiveness of their anticorrosive properties depends on parameters such as precursor concentration, deposition and drying times, heat treatment, the number of immersions, aging time, and the pH of the solution [16–18].

Titanium dioxide (TiO<sub>2</sub>) is valued for its stability, good optical absorption, and low cost, making it ideal for photocatalytic applications. Its anatase phase is especially noted for its high photocatalytic activity, which

**Table 1:** Nomenclature for the organic-inorganic hybrid sol-gel coatings.

| HYBRID ORGANIC-INORGANIC SOL-GEL |           |                            |           |               |                                    |
|----------------------------------|-----------|----------------------------|-----------|---------------|------------------------------------|
| SUBSTRATE                        | PRECURSOR | TITANIUM SOURCE            | SOLUTIONS | COATINGS      | COATINGS AFTER SALT SPRAY EXPOSURE |
| Cu                               | –         | –                          | –         | S1 (uncoated) | SE1 (uncoated)                     |
|                                  | GPTMS     | –                          | G1        | GC1           | GCE1                               |
|                                  |           | TiO <sub>2</sub> particles | G2        | GC2           | GCE2                               |
|                                  |           | TTIP                       | G3        | GC3           | GCE3                               |

is of benefit for self-cleaning and antibacterial materials. Doping with elements such as silicon (Si), zirconium (Zr), vanadium (V), and lanthanum (La) enhances these properties and improves TiO<sub>2</sub> stability under extreme conditions and visible light. Additionally, the superhydrophobic properties of TiO<sub>2</sub> facilitate surface cleaning and increase corrosion resistance, due to anatase phase stabilization and reduced electron-hole pair recombination [19–22]. The coexistence of organic and inorganic components in the gel results in synergistic properties, such that the inorganic part contributes to mechanical strength and thermal stability, while the organic part can supply functionalities such as antibacterial properties [23, 24]. Hybrid sol-gel coatings are classified into two types (Class I and Class II), based on the nature of the interactions between their organic and inorganic parts [25]. In Class I hybrid sol-gel coatings, metal oxide particles (e.g., TiO<sub>2</sub> particles [26]) are embedded in the organic matrix through weak bonds without covalent interaction. In Class II coatings, the metal oxide particles are interspersed throughout a network formed by organic and inorganic compounds linked via covalent, ionic-covalent, or Lewis's acid-base bonds [27].

This paper introduces a novel coating with activated TiO<sub>2</sub> and demonstrates a novel approach to enhancing copper corrosion resistance by comparing the effectiveness of three sol-gel matrix hybrid coatings. Below, Table 1 is included and presented, outlining the nomenclature of the organic-inorganic sol-gel hybrid coatings used in this research. The three coatings included one based on 3-glycidoxypyltrimethoxysilane (GPTMS – GC1) and two different classes of hybrid coatings derived from G1 and activated with titanium. Class I incorporated crystallized TiO<sub>2</sub> particles in the matrix (GC2), while Class II used the liquid precursor titanium (IV) isopropoxide (TTIP – G3). In this study, the corrosion resistance of three coatings was assessed using salt-spray tests following ASTM B117 standards and using electrochemical impedance spectroscopy (EIS). Detailed analyses were performed through profilometry, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), and X-ray diffraction (XRD) to characterize the coatings' structures and properties. The results highlighted the superior performance of a hybrid organic-inorganic coating based on GPTMS combined with TiO<sub>2</sub> particles (GC2) and another based on GPTMS combined with TTIP (GC3). Corrosion testing involved Nyquist plots and Tafel curves to accurately adjust the electrochemical parameters in these organometallic systems. Additionally, potentiodynamic polarization provided Tafel slopes and corrosion current density, corrosion potential, and corrosion rate data for both the substrate and the coatings. The EIS analysis yielded Nyquist diagrams for all conditions, offering comprehensive data for future applications and research on copper corrosion protection.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

The following chemicals were used: (3-glycidyloxypropyl) trimethoxysilane (C<sub>9</sub>H<sub>20</sub>O<sub>5</sub>Si) (GPTMS, 98%, Aldrich); isopropanol ((CH<sub>3</sub>)<sub>2</sub>CHOH, 99%, Aldrich); acetic acid (CH<sub>3</sub>CO<sub>2</sub>H, 100%, Sigma-Aldrich); acetylacetone (CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>, 99%, Sigma-Aldrich); methanol (CH<sub>3</sub>OH, 99%, Aldrich); and titanium (IV) isopropoxide (TTIP, Ti [OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, 97%, Sigma-Aldrich).

### 2.2. Preparation and characterization of the TiO<sub>2</sub> particles

Titanium dioxide particles were synthesized using titanium isopropoxide as the precursor. In a beaker, 8.85 ml (about 0.3 oz) of isopropanol were mixed with 3.3 ml (about 0.11 oz) of titanium (IV) isopropoxide, with a pH level of 2–3. The contents were stirred for 15 minutes at room temperature. Then 3 ml (about 0.1 oz) of acetic acid were added to the mixture. The stirring was stopped after 30 minutes. The reaction product was removed and dried in an oven at 393 K for 24 h. The product obtained was ground, washed by centrifugation with deionized water for 5 minutes at 8000 rpm, and then calcined at 713 K for 2 h and cooled inside the oven.

The formation of  $\text{TiO}_2$  particles was confirmed through SEM-EDS analysis and X-ray diffraction (XRD). X-ray diffraction analysis was performed on the powder to determine the phase of the synthesized particles, using a Bruker D8 Advance Eco instrument in a  $2\theta$  range of  $10^\circ$  to  $65^\circ$ , with a scanning rate of  $4^\circ\text{min}^{-1}$ .

### 2.3. Synthesis of organic base sol (G1) and titanium-activated hybrid inorganic-organic sols (G2 and G3)

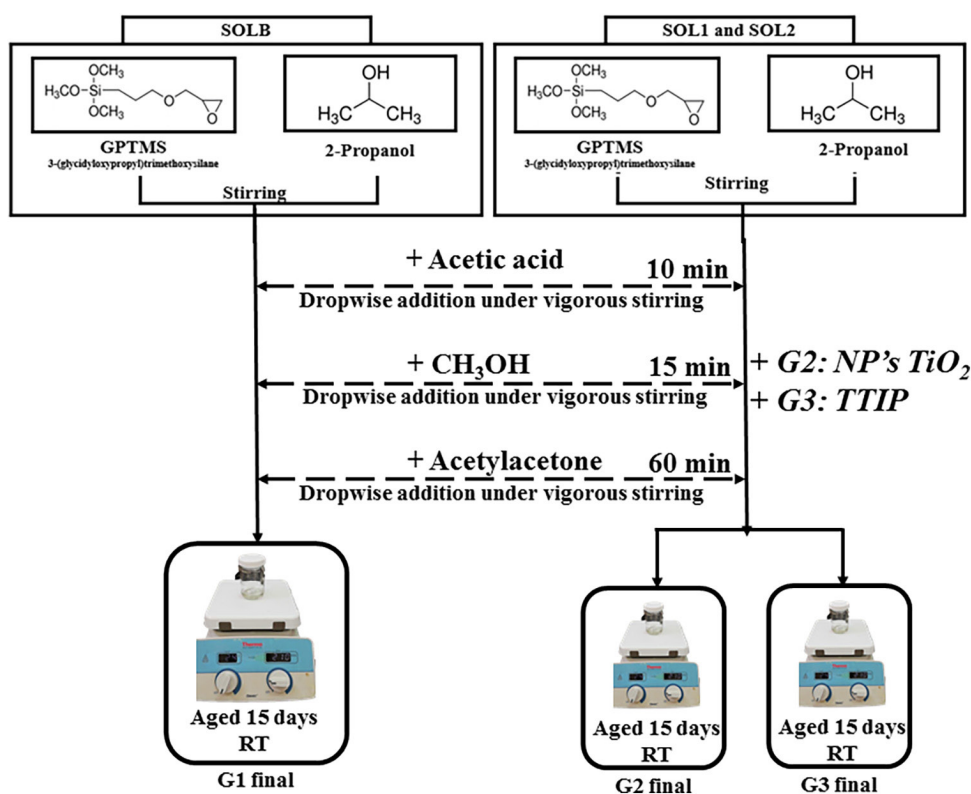
Three organic-inorganic hybrid solutions – SOLB (G1), SOL1 (G2), and SOL2 (G3) – were prepared, as shown in Figure 1. All the reactions were conducted dropwise at 333 K. G1 was an organosiloxane solution prepared by stirring a mixture of 0.01 M GPTMS and 0.1 M 2-propanol at 100 rpm for 10 min. Then, 0.1 M acetic acid was added, and the mixture was stirred for 10 min. Next, 0.3 M methanol was added and stirred for 15 min. Finally, 0.01 M acetyl acetone was added while stirring for about 60 min. For G2, previously synthesized  $\text{TiO}_2$  particles were added to the mixture, along with acetic acid. For G3, 0.01 M of TTIP (titanium (IV) isopropoxide) was added, along with acetic acid. The solutions were aged for 15 days.

### 2.4. Coating preparation through dip-coating technique

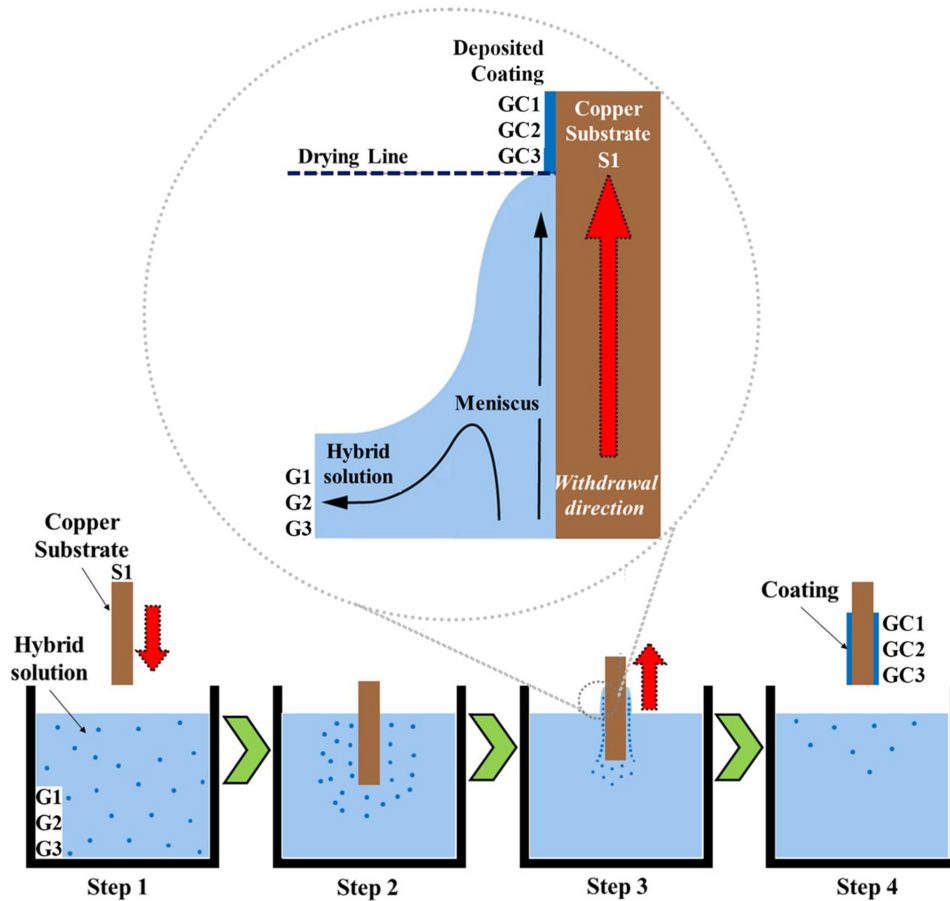
To prepare solutions G2 and G3, the same method described earlier was employed (shown in Figure 1 and detailed in Table 1). The inorganic-organic hybrid coating was deposited onto copper substrates (S) measuring 75 mm (about 2.95 in)  $\times$  25 mm (about 0.98 in) and 1 mm (about 0.04 in) in thickness. The surfaces had been polished with 600-grit SiC paper. The samples were ultrasonically cleaned with 2-propanol for 10 min prior to the deposition procedure. Details of the immersion coating technique were published previously [28]. Figure 2 illustrates the immersion coating technique, and the key steps followed to form a coating on the copper surface. Three different coatings were produced: G1, G2 and G3; their deposition conditions are specified in Table 2. One substrate (S1) was left uncoated as a reference sample.

### 2.5. Coating effectiveness via salt-spray test

The coatings were subjected to the conditions outlined in Table 3, following the ASTM B117 standard [29]. The salt-spray test is commonly used to assess the corrosion resistance of metallic materials, especially those to be exposed to marine environments with high saline humidity. Figure 3 illustrates a typical setup for a fog nozzle with a single-atomizer tower cabinet (Atlas Electric Devices model SF500).



**Figure 1:** Procedure for the experimental preparation of the three hybrid organic-inorganic GPTMS-based sols (G1, G2, and G3).



**Figure 2:** Diagram of the main steps of deposition by the dip-coating technique.

**Table 2:** Deposition conditions of the dip-coating technique.

| PARAMETERS                     | VALUE                 |
|--------------------------------|-----------------------|
| Substrate                      | Cu                    |
| Substrate temperature          | Room temperature (RT) |
| Immersion/extraction speed     | 70 mm·s <sup>-1</sup> |
| Immersion displacement         | 37 mm                 |
| Number of immersion cycles     | 10 cycles             |
| Drying time every 3 immersions | 10 min                |
| Final drying time              | 24 h                  |
| Drying temperature             | 120°C                 |

**Table 3:** Salt spray test conditions (ASTM B117 standard).

| PARAMETERS                                      | VALUE                      |
|-------------------------------------------------|----------------------------|
| Distance between specimens                      | 2 cm                       |
| Position of specimens during exposure           | 20°                        |
| Salt solution with 95 parts of H <sub>2</sub> O | 5 ± 1 part by mass of NaCl |
| Atomization temperature                         | 35°C (95°F)                |
| pH                                              | 6.5 to 7.2                 |
| Exposure time                                   | 5 days                     |

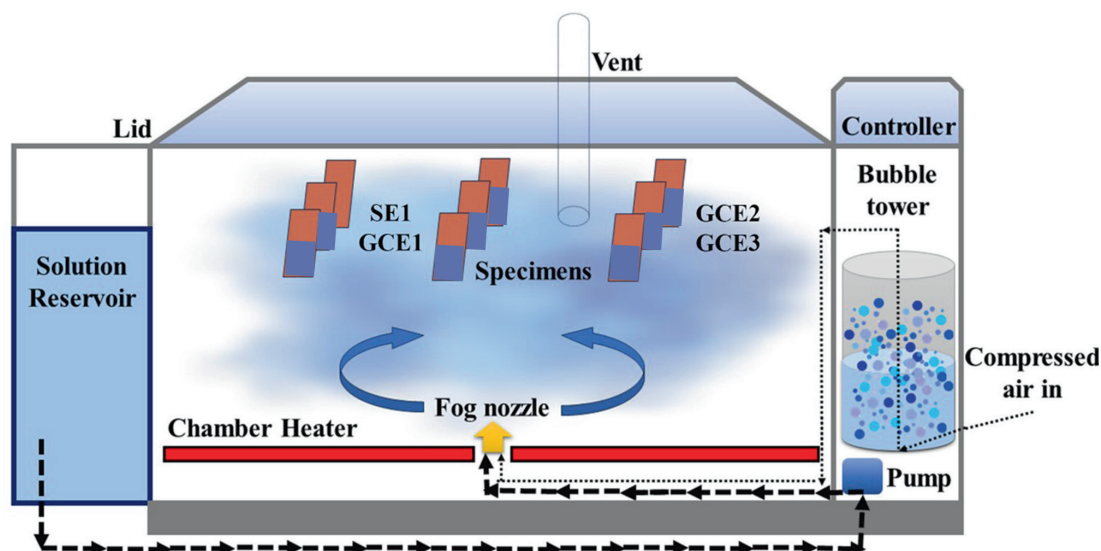


Figure 3: Arrangement of the fog collector, based on the ASTM B117 standard.

Table 4: Composition of the synthetic brine.

| COMPOUND                       | NOMENCLATURE                         | COMPOSITION/g·L <sup>-1</sup> |
|--------------------------------|--------------------------------------|-------------------------------|
| Sodium chloride                | NaCl                                 | 106.5789                      |
| Calcium chloride dihydrate     | CaCl <sub>2</sub> ·2H <sub>2</sub> O | 4.4773                        |
| Magnesium chloride hexahydrate | MgCl <sub>2</sub> ·6H <sub>2</sub> O | 2.061                         |

## 2.6. Linear polarization and electrochemical impedance spectroscopy testing

EIS tests were conducted on the substrate (S1), a hybrid organic-inorganic coating based on the precursor GPTMS combined with TiO<sub>2</sub> particles (GC2), and on another based on the precursor GPTMS with TTIP (GC3), using a synthetic brine whose composition is detailed in Table 4.

For the corrosion tests, a commercial electrochemical workstation from *Solartron* was used, equipped with *CorrWare* software for electrochemical data acquisition. The experiments were conducted at room temperature using the described electrolyte (Table 4). The electrochemical cell consisted of a classic three-electrode system, which contained a reference electrode (Ag/AgCl), a high-purity graphite counter-electrode ©, and a working electrode made up of the samples to be evaluated, which were: the substrate (S1), a hybrid organic-inorganic coating based on GPTMS combined with TiO<sub>2</sub> particles (GC2), and another based on GPTMS combined with TTIP (GC3). These samples were mounted in a Teflon tube, with each sample exposing an area of 1 cm<sup>2</sup> to the electrolyte.

Potentiodynamic tests were conducted by applying a potential of  $\pm 250$  mV relative to the open circuit potential for each evaluation condition, with a scan rate of 0.16 mV·s<sup>-1</sup>. The applied potential and current density data were recorded using the potentiostat's data acquisition system. Electrochemical impedance spectroscopy (EIS) tests were performed over a frequency range of 1 mHz to 100 kHz, using a  $\pm 10$  mV sinusoidal perturbation. These tests were conducted under the same conditions for all three samples.

## 2.7. Morphological and structural characterization

The inorganic-organic hybrid coatings were first analysed using scanning electron microscopy (JEOL JSM-6701F) to figure out surface morphology, elemental composition (via EDS), and coating thickness. Optical profilometry (Bruker Contour GTK Profilometer, 3D) was used to characterize surface topography; the scanning areas were 10 × 10 μm<sup>2</sup>. The surface topographies (2D and 3D), arithmetic roughness, and arbitrary length profiles of the samples were examined in non-contact mode. Subsequently, phase identification was conducted through x-ray diffraction (Bruker, D8 Advance) with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) at a grazing angle of 0.5°, with a step size of 0.02° and a step time of 0.3 s.



### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of TiO<sub>2</sub> particles

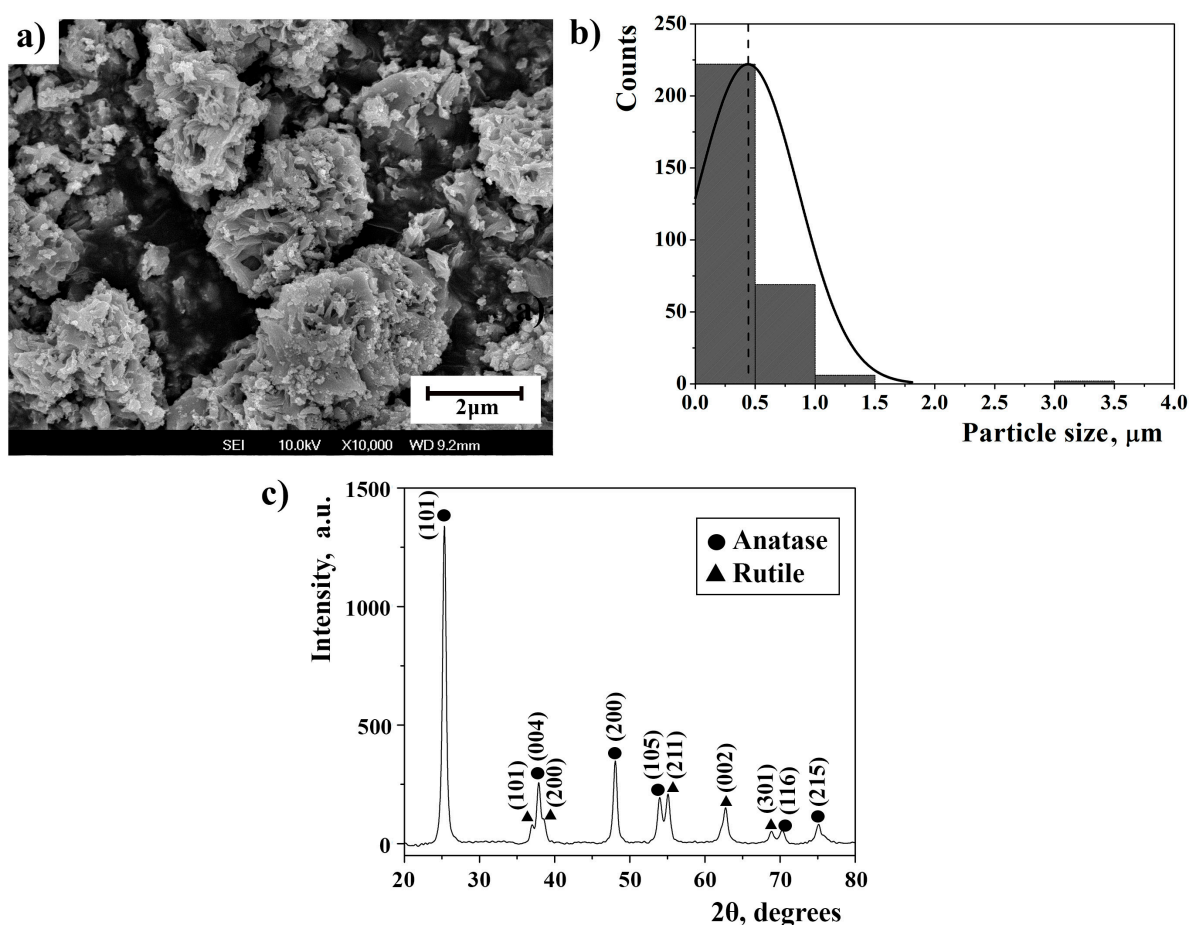
SEM mapping of the agglomerated/aggregated TiO<sub>2</sub> particles was conducted (Figure 4a), and a histogram was produced based on an analysis of 300 measurements of these particles (Figure 4b). The particle size distribution reflects the relative proportions of the assorted sizes in the sample, which range from 0.25  $\mu\text{m}$  to 1.5  $\mu\text{m}$ , with an average size of 0.439  $\mu\text{m}$ , going with a coral-like structure. The variability in particle size within the hybrid matrix is needed to effectively fill gaps of varied sizes. Small particles might not be able to adequately fill large voids, while large particles can. Thus, this diversity ensures the complete and uniform filling of gaps and enhances the integrity and uniformity of the coating. Preventing voids is crucial to avoid structural weakening and to protect against undesirable external agents, such as moisture [30–31]. The X-ray diffraction pattern of the TiO<sub>2</sub> particles is shown in Figure 4c. The peaks appearing there correspond to two phases: an anatase phase (according to JCPDS-ICDD card: 21-1272) and a rutile phase (according to JCPDS-ICDD card: 75-1537), with anatase being the predominant phase in the sample [32–35].

#### 3.2. Characterization of the hybrid coatings

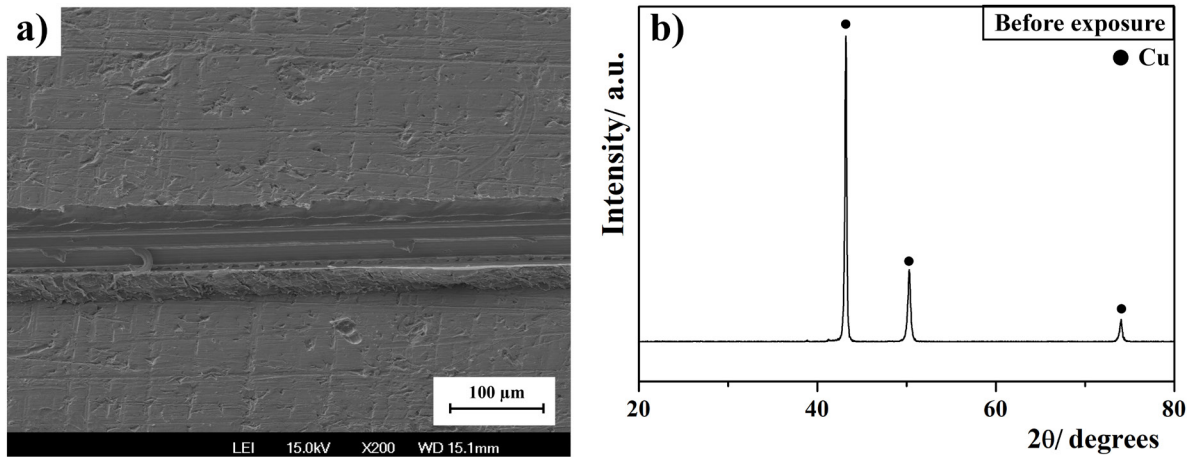
##### 3.2.1. Uncoated substrate (S1)

Figure 5a shows a SEM image of the surface used as the substrate for the coatings (S1) in this study. The scratches indicate the absence of coating. In the x-ray diffraction (XRD) pattern (Figure 2b), a structure corresponding to copper is seen, following JCPDS No. 003–1018 pattern [36].

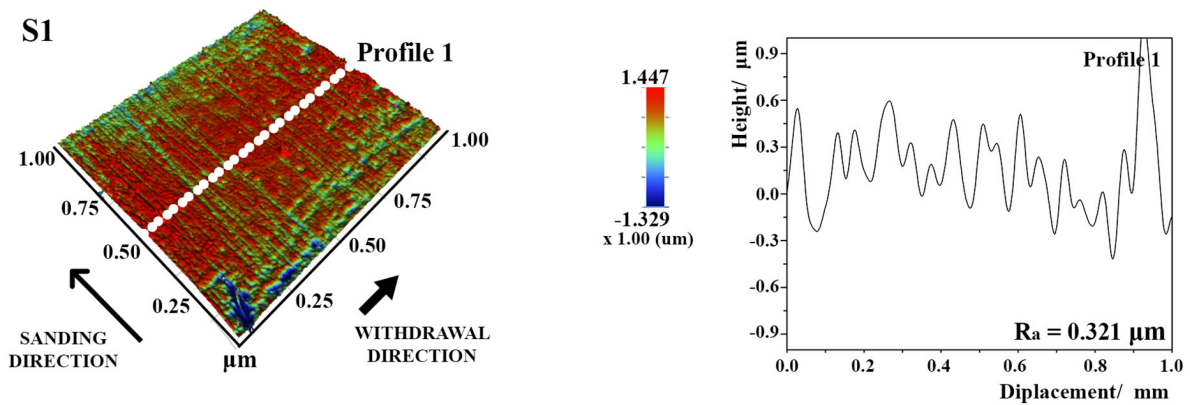
Figure 6 presents the topographical analysis of the uncoated substrate; the thickness and surface roughness values of the different coatings are detailed in Table 5. According to an earlier study conducted by Krechetnikov and Homsy [37], applying coatings by immersion on a polished plate is not the best choice; they showed that in rough grooves, a certain amount of the sol-gel gets trapped, which helps to anchor the coating. Therefore, to maximize the coating anchoring efficiency of the sample, the immersion withdrawal was



**Figure 4:** Analysis of the TiO<sub>2</sub> particles: (a) a scanning electron micrograph, (b) a graph showing standard normal distribution of particle size, (c) the X-ray diffraction pattern.



**Figure 5:** Analysis of the copper substrate surface (S1): (a) a scanning electron micrograph, and (b) the X-ray diffraction pattern.



**Figure 6:** Surface map of the copper substrate surface (S1) and representative cross-section plot.

**Table 5:** Film thickness measurements and surface roughness parameters before exposure to salt spray test conditions.

| SAMPLE | FILM THICKNESS/ $\mu\text{m}$ | $Ra/\mu\text{m}$ |
|--------|-------------------------------|------------------|
| S1     | —                             | $0.321 \pm 0.02$ |
| GC1    | $0.777 \pm 0.3$               | $0.162 \pm 0.04$ |
| GC2    | $2.054 \pm 0.1$               | $0.247 \pm 0.02$ |
| GC3    | $3.774 \pm 0.23$              | $0.197 \pm 0.03$ |

performed perpendicular to the direction of the sanding. As shown in profile 1 (Figure 6), the topography exhibited an arithmetic roughness of  $0.321 \pm 0.2 \mu\text{m}$ .

### 3.2.2. Surface roughness analysis

Figure 7a (GC1) and Figure 4c (GC3) show a coating distribution of  $0.162 \pm 0.04 \mu\text{m}$  and  $0.197 \pm 0.03 \mu\text{m}$ , respectively, with a trend toward a lower average surface roughness. In profile 3, an increase in roughness is observed because the coating contains  $\text{TiO}_2$  particles dispersed in the organic matrix, which results in a non-uniform distribution of particles that directly affects the roughness value (Figure 7b). On the other hand, the coating in Figure 7c exhibits a densely packed compact layer with an improved surface finish ( $0.212 \pm 0.04 \mu\text{m}$ ) [38].

In Figures 7a-c, stripes perpendicular to the direction of substrate withdrawal during the dip-coating technique are observed. This defect appears at regular intervals along the coated substrate and is due to three inherent parameters: different extraction speeds and viscosities, and the different techniques used until the combination that worked best for a specific application was found [39].

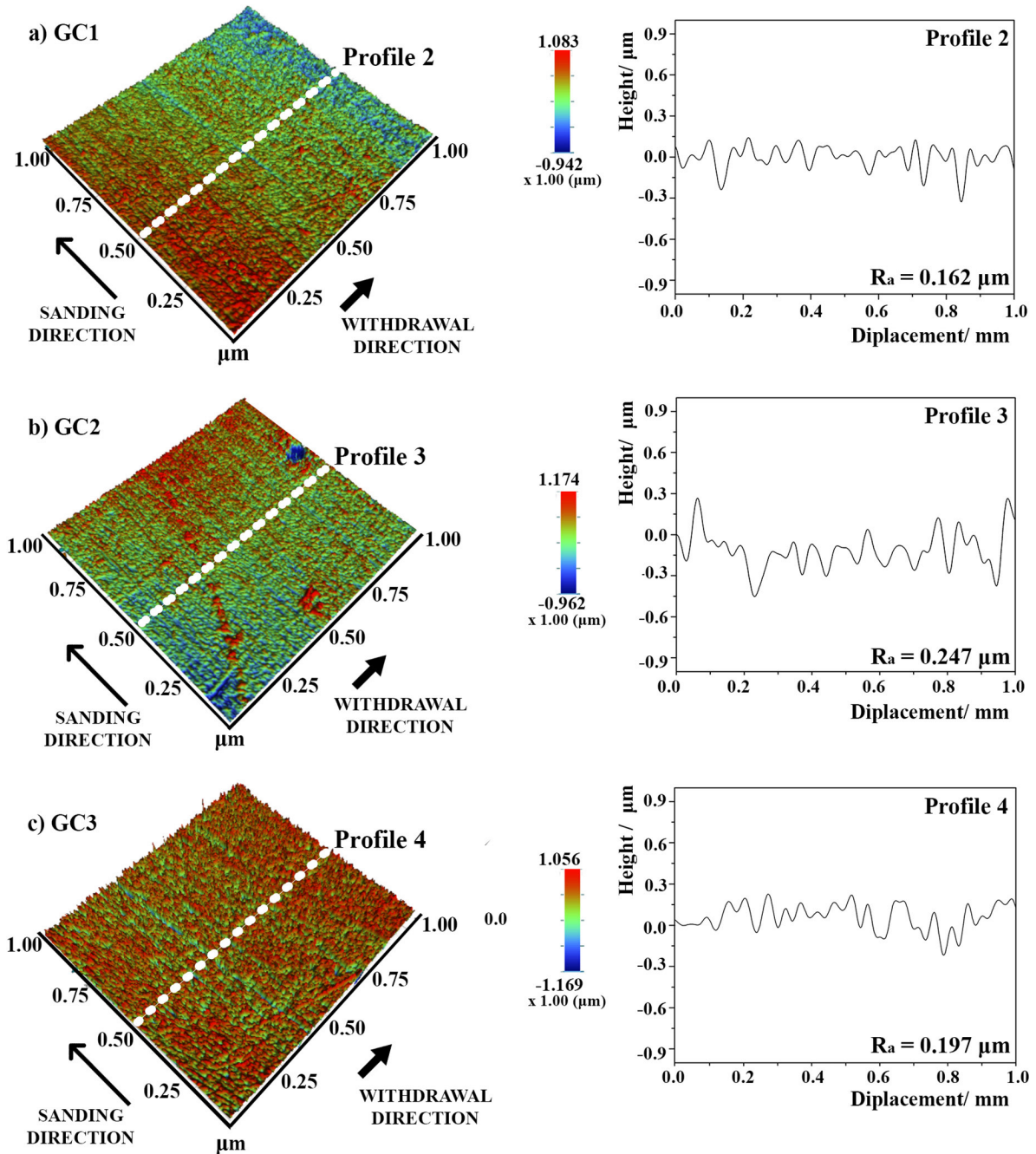
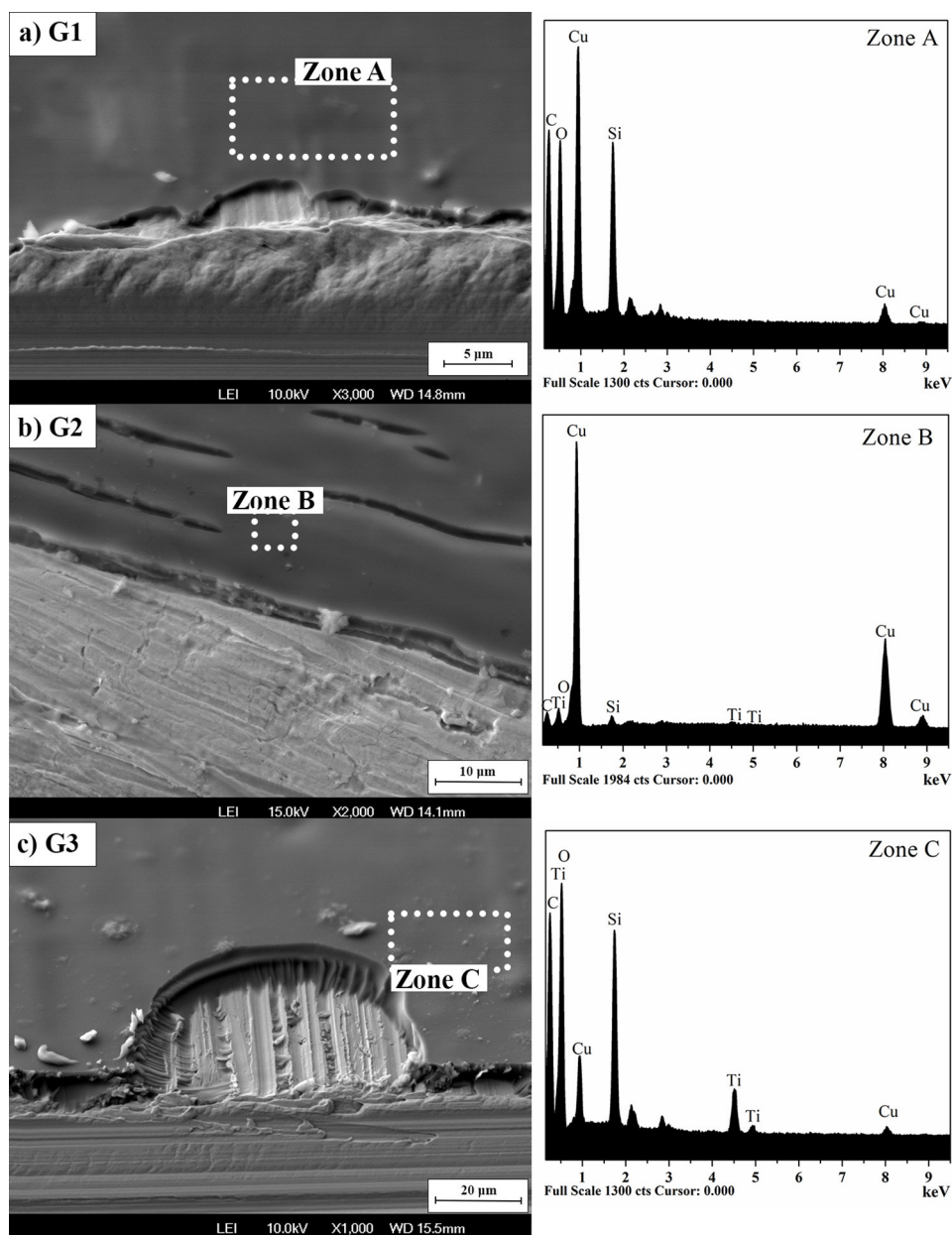


Figure 7: Surface maps of the hybrid organic-inorganic films and their representative cross-section plots.

### 3.2.3. Surface morphologies of the coatings and elemental surface analyses

In Figure 8, the surface morphologies of the coatings can be observed, accompanied by characteristic EDS spectra. According to VEGA-MORÓN *et al.* [40], this methodology was employed to accurately determine the coating thickness. The coating thickness results are summarized in Table 5. GC1 has a thickness of  $0.777 \pm 0.3 \mu\text{m}$ , GC2 a thickness of  $2.054 \pm 0.1 \mu\text{m}$ , and GC3 a thickness of  $3.774 \pm 0.23 \mu\text{m}$ . GC1 and GC3 exhibit a uniform structure without noticeable cracks. The coating thickness is related to the withdrawal speed applied during the coating process (see Table 2), as shown by the Landau-Levich equation [41]. The incorporation of  $\text{TiO}_2$  particles (G2) and TTIP (G3) into the organic matrix (G1) resulted in a significant increase in thickness, doubling it (GC2) and tripling it (GC3), respectively. GC2 displays surface cracks and a laminar interlocking pattern perpendicular to the substrate, as shown in Figure 8c. Nanocomposites combine organic and inorganic phases through non-covalent interactions, such that one phase forms a network via covalent bonds, while the other disperses at the nanoscale in the hydrogel, interacting weakly with the network. Class I hybrid hydrogels incorporate inorganic particles into an organic matrix formed by organic, rather than inorganic, polymerization. The elemental surface analyses of the



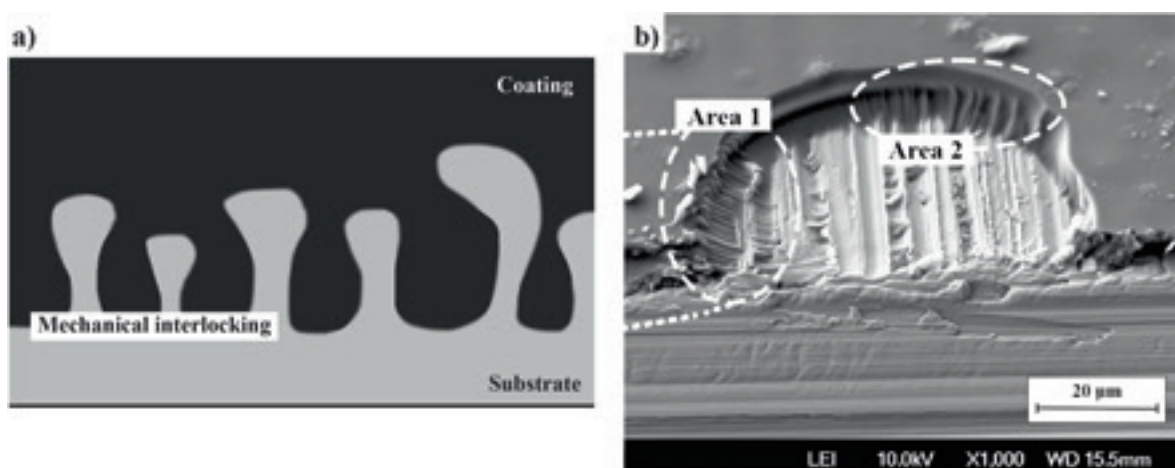


**Figure 8:** Scanning electron micrographs and EDS spectra obtained for the marked surfaces of GC1, GC2, and GC3.

samples revealed similar patterns in all the coatings. In Figure 8a, GC1 shows the presence of C (0.28 keV), O (0.53 keV), and Si (1.89 keV). The Si peak can be attributed to the organic precursor GPTMS, and C shows the organic compounds derived from it. These inorganic particles may be trapped or weakly adsorbed in the network, acting as cross-linking nodes. Si, with low electrophilicity and zero unsaturation, and Ti, with higher unsaturation, can cause surface cracking in  $\text{TiO}_2$  particles if they are not fully incorporated, as noted by FALARAS *et al.* [38]. Particle size distribution and discrepancies in shrinkage during drying generate internal stresses that disrupt the uniformity of the coating and cause cracking. To prevent the formation of disconnected areas and gaps that reduce the effectiveness of the coating, it is crucial to maintain structural continuity while addressing fractures and interstices between particles [42]. However, in GC3, a phenomenon of laminar and perpendicular mechanical interlocking is observed (see Figure 9), which will be explained in the next section.

### 3.2.4. Mechanical interlocking and coating adhesion

Figure 8c shows a GC3 coating that confirms the uniform distribution of the inorganic Ti precursor (0.452 keV, 4.508 keV, and 4.931 keV) in the organometallic hybrid matrix. For GC3, the EDS spectra reveal peaks corresponding to Ti (0.38 keV, 4.45 keV), C (0.28 keV), O (0.53 keV), and Si (1.89 keV), confirming the presence of Ti in the Class II hybrid matrix. Hybrid hydrogels in which organic and inorganic domains are covalently



**Figure 9:** (a) The mechanical interlocking mechanism and (b) mechanical interlocking phenomena in a scanning electron micrograph of GC3.

bonded are classified as Class II hybrid hydrogels [42]. Compared to GC2 (Figure 8b), the image of GC3 shows a more homogeneous distribution of the inorganic TTIP precursor on the surface, compared to the  $\text{TiO}_2$  particles in GC2, as evidenced by the higher intensity of Ti peaks in zone C. In all cases, the stable Si-C bonds linking the organic and inorganic parts are confirmed by the EDS spectra.

The hydrolysis and condensation of alkoxy silane groups result in the formation of siloxane bonds between the different silicon-containing precursors, ensuring the solidification of the hydrogel. The chemical introduction of a silyl group into an organic molecule from GPTMS [43], known as silylation, forms covalent bonds that facilitate the anchoring mechanism. This mechanism, illustrated in Figure 9a, is crucial for ensuring a strong and stable bond between the substrate and the coating. According to the mechanical adhesion theory, effective adhesion is achieved when a coating penetrates and adheres to a rough substrate surface. This penetration enhances the contact area between the two materials, allowing for a greater number of molecular bonding interactions. Thus, the coating mechanically interlocks with the substrate, creating a more robust connection [44].

In Figure 9b, this interlocking effect is evident in areas 1 and 2, where the GC3 coating, which has effectively penetrated the substrate surface, shows superior adhesion compared to that of GC1 and GC2. The presence of TTIP in the GC3 formulation contributed to this improved performance by providing favorable rheological properties, which facilitated better penetration and bonding with the substrate.

The establishment of stronger interactions between inorganic and organic networks, ideally through covalent bonds, can prevent phase separation, even on a nanoscale, giving the Class II hybrid, GC3 hydrogel perfect homogeneity on a micrometric scale. The effects of this homogeneity are reflected in good optical transparency and a significant improvement in mechanical properties [45].

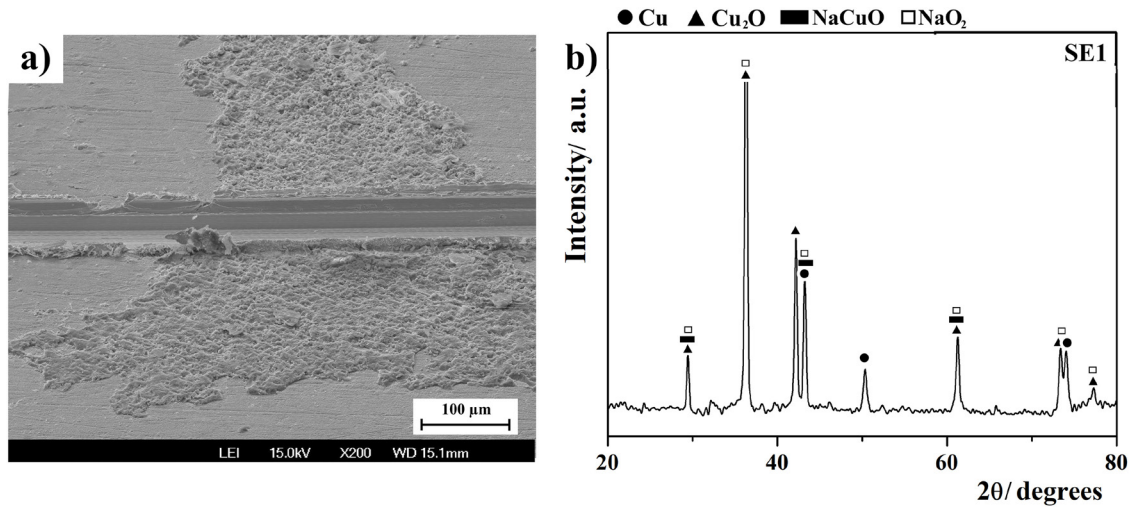
### 3.3. Copper substrate behaviour under salt-spray test conditions

#### 3.3.1. Copper substrate (SE1)

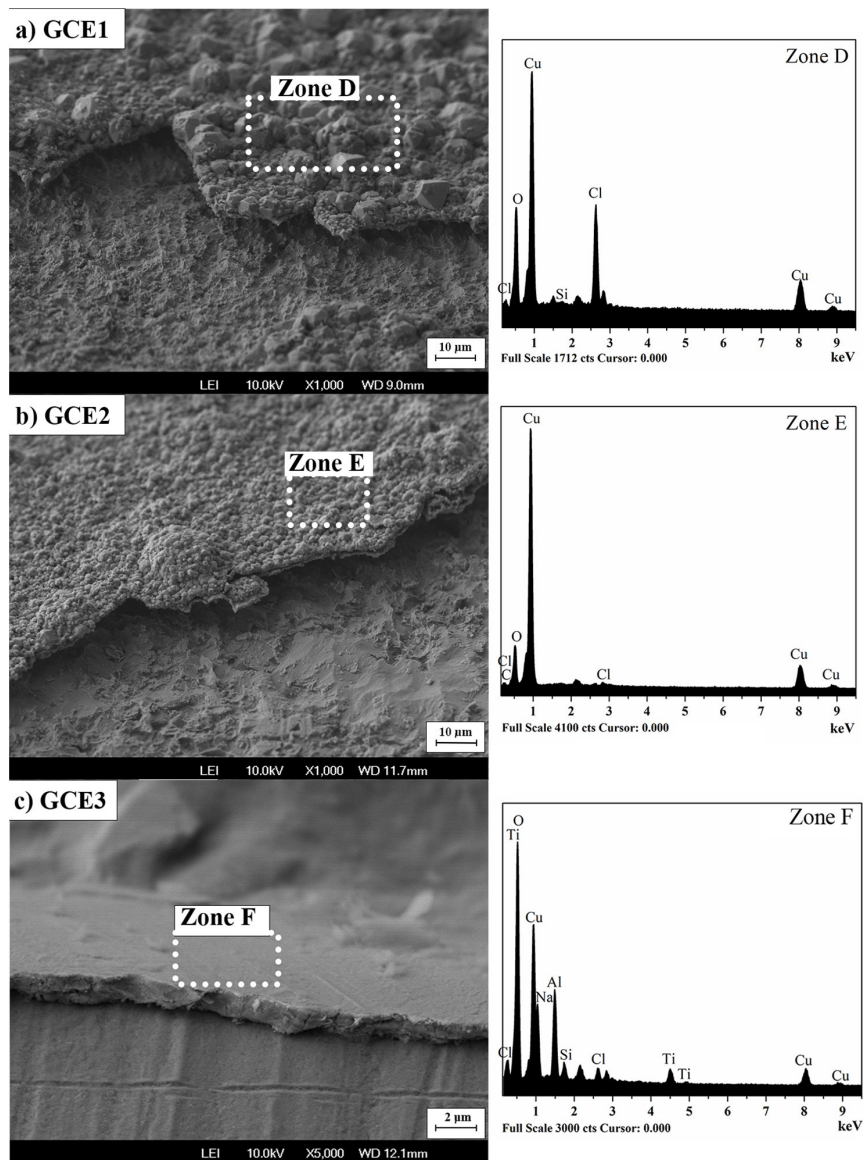
The copper substrate exposed to salt-spray conditions (SE1) shows significant surface changes, including the formation of by-products and oxides that were visually detected in Figure 10a. These changes were analysed using X-ray diffraction (XRD) (Figure 10b). Compounds such as Cu,  $\text{Cu}_2\text{O}$ ,  $\text{NaCuO}$ , and  $\text{NaO}_2$  were identified, showing the nature and composition of the products formed on the copper substrate surface. Cu is present due to the copper substrate, and  $\text{Cu}_2\text{O}$  indicates the formation of copper oxide on the surface. The occurrence of  $\text{NaCuO}$  and  $\text{NaO}_2$  is also a consequence of substrate oxidation, induced by elements such as Na in the salt-spray [46].

#### 3.3.2. Coating behaviour under salt-spray test conditions

In Figure 11, SEM images of the coatings after exposure to salt-spray are presented for GCE1, GCE2, and GCE3. In GCE1 and GCE2 (Figure 11a and 11b, respectively), precipitates formed on the surface, significantly altering their morphology, and causing phase segregation between the coating thickness and the growth of precipitates (see Table 6). This resulted in a total thickness of  $5.862 \pm 0.20 \mu\text{m}$  in GCE1 and  $2.377 \pm 0.2 \mu\text{m}$  in GCE2. In contrast, GCE3 exhibits a uniform, crack-free surface (Figure 11c). Improving the roughness to  $0.221 \pm 0.23 \mu\text{m}$ , the incorporation of metallic precursors such as  $\text{TiO}_2$  (G2) and TTIP (G3) into G1 prevents this deterioration. GCE3 (Figure 12c) displays a dense layer without precipitates, resulting in an enhanced roughness



**Figure 10:** Scanning electron micrograph and X-ray diffraction pattern for the surface of the copper substrate (SE1) exposed to salt spray test conditions.

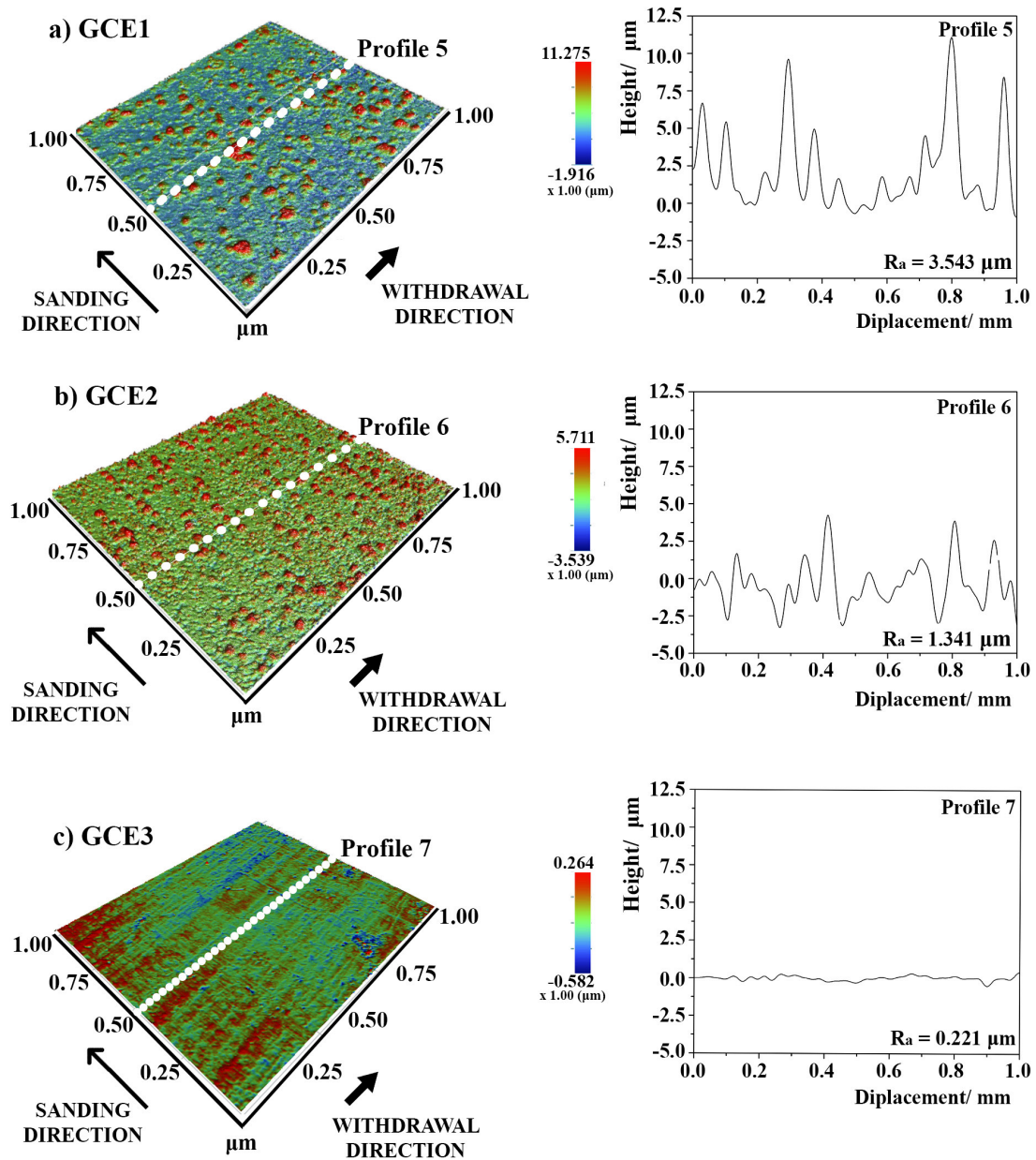


**Figure 11:** Scanning electron micrographs and EDS spectra for the surfaces of GCE1, GCE2, and GCE3, exposed to salt spray test conditions.



**Table 6:** Film thickness measurements and surface roughness parameters after exposure to salt spray test conditions.

| SAMPLE | FILM THICKNESS/ $\mu\text{m}$ | PRECIPITATE THICKNESS GROWTH/ $\mu\text{m}$ | $R_a/\mu\text{m}$ |
|--------|-------------------------------|---------------------------------------------|-------------------|
| SE1    | —                             | —                                           | $0.621 \pm 0.3$   |
| GCE1   | $1.104 \pm 0.05$              | $4.759 \pm 0.1$                             | $3.543 \pm 0.04$  |
| GCE2   | $0.581 \pm 0.02$              | $1.796 \pm 0.07$                            | $1.341 \pm 0.03$  |
| GCE3   | $1.086 \pm 0.06$              | —                                           | $0.221 \pm 0.03$  |

**Figure 12:** Surface maps and representative cross-section plots of the hybrid organic-inorganic films after exposure to salt spray test conditions.

[47]. When the profilometry data were correlated with the EDS spectra for zones E and G (Figures 11b and 13c), a decrease in the organic part (Si) and an absence of  $\text{TiO}_2$  distribution were seen. In contrast, in zone F (Figure 11c), the inorganic precursor TTIP was detected at a higher concentration, as showed by the Ti peaks. These results show that the liquid TTIP in the hybrid system formed a compact and densely packed coating that served as a barrier that prevented direct contact between the copper and exposure to the salt-spray.



The average roughness of the coatings was calculated using optical profilometry imaging (Figure 12). GCE1 and GCE2 (Figures 12a and 12b) show precipitates with an average roughness of  $3.543 \pm 0.04 \mu\text{m}$  and  $1.341 \pm 0.03 \mu\text{m}$ , respectively, suggesting surface deterioration. GCE3 (Figure 12c) displays a dense layer without precipitates, resulting in an enhanced roughness [47].

Exposure to salt-spray produced significant changes in the GCE1 and GCE2 coatings, as seen in Figure 13. On the surface of GCE1, precipitates with an average size of  $4.759 \pm 0.1 \mu\text{m}$  are observed, while in GCE2, the average size is  $1.796 \pm 0.07 \mu\text{m}$  (Figure 13d). These results highlight the variability in the uniformity and size of the precipitates due to exposure to the saline environment; they are approximately four times larger in GCE1 than in GCE2.

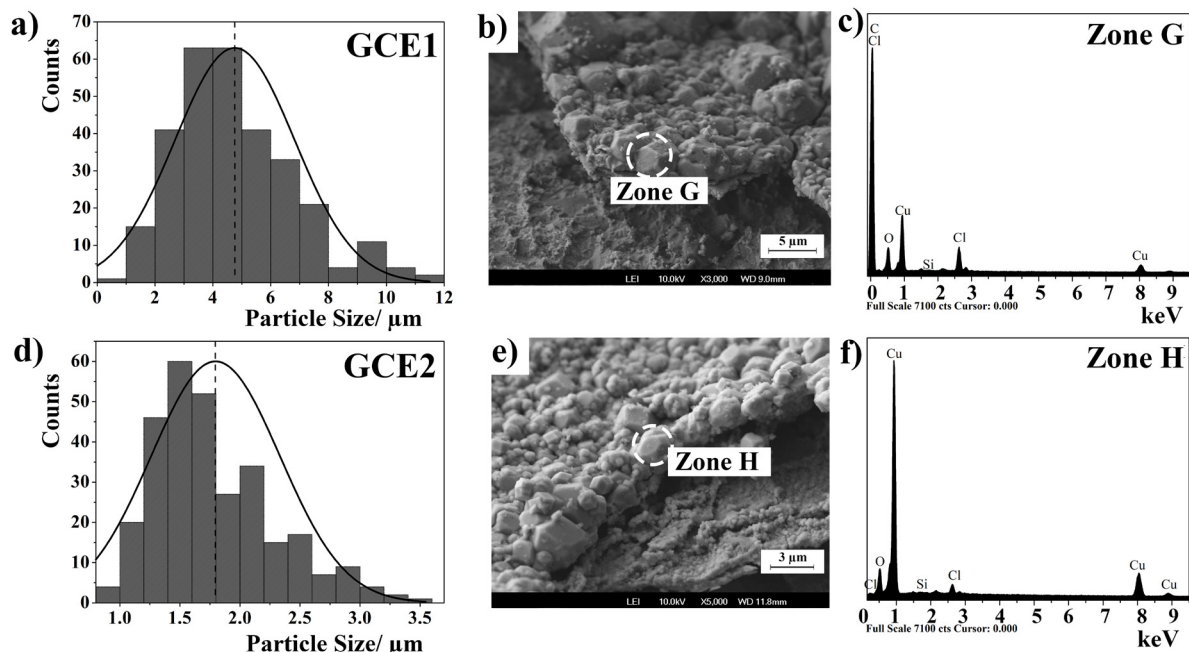
Elemental analysis by EDS (Figure 13c and f) reveals silicon (Si) and copper (Cu), which came from the compounds used in the coating and the substrate, respectively. Carbon © is associated with the organic compounds in the sample. Oxygen reacts with silicon (Si) and copper (Cu), forming oxides on the surface. The EDS spectra in Figure 11(a–b) show Cl (0.3 keV and 2.6 keV), O (0.53 keV), and Si (1.89 keV) on the coated surfaces, resulting from the influence of the saline solution. Corrosion occurred due to precipitates formed from reactions between the saline solution components and the coating surfaces. The presence of  $\text{TiO}_2$  particles in GC2 and the direct contribution of elements from the saline solution led to a transition from diffusion bonding to chemical bonding [31]. It has been reported that the substitution of  $\text{Ti}^{4+}$  by  $\text{Si}^{4+}$  and  $\text{Cu}^{2+}$  within the  $\text{TiO}_2$  lattice reduces the rate of electron-hole pair recombination. This reduction in the recombination rate is responsible for the observed decrease in the degradation rate, enhancing the overall durability of the coating [48–49].

### 3.4. Effect of salt-spray exposure on hybrid coatings

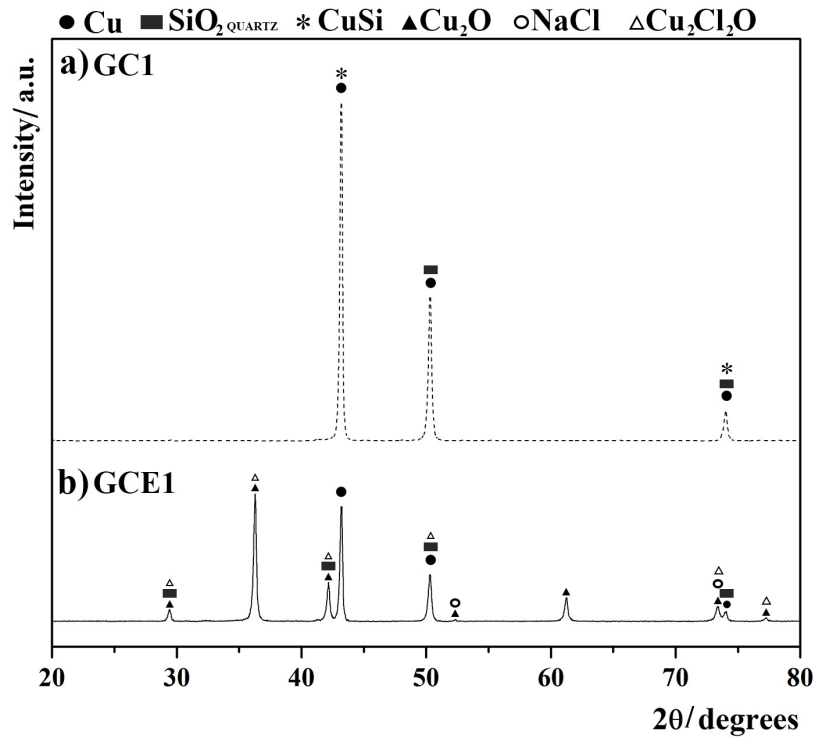
The results of the XRD analysis of GC1, GC2, and GC3 before and after exposure to salt-spray are presented in Figures 14, 15, and 16, respectively.

In Figure 14, GC1 exhibits diffraction peaks that reflect the formation of crystalline  $\text{SiO}_2$  due to the oxidation of silicon from GPTMS on the copper substrate. GCE1 shows corrosion on the copper surface, which holds oxides such as  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{Cl}_2\text{O}$ , due to the preferential oxidation of silicon, which led to the formation of copper silicide ( $\text{CuSi}$  or  $\text{SiCu}$  (silicon copper compound)).

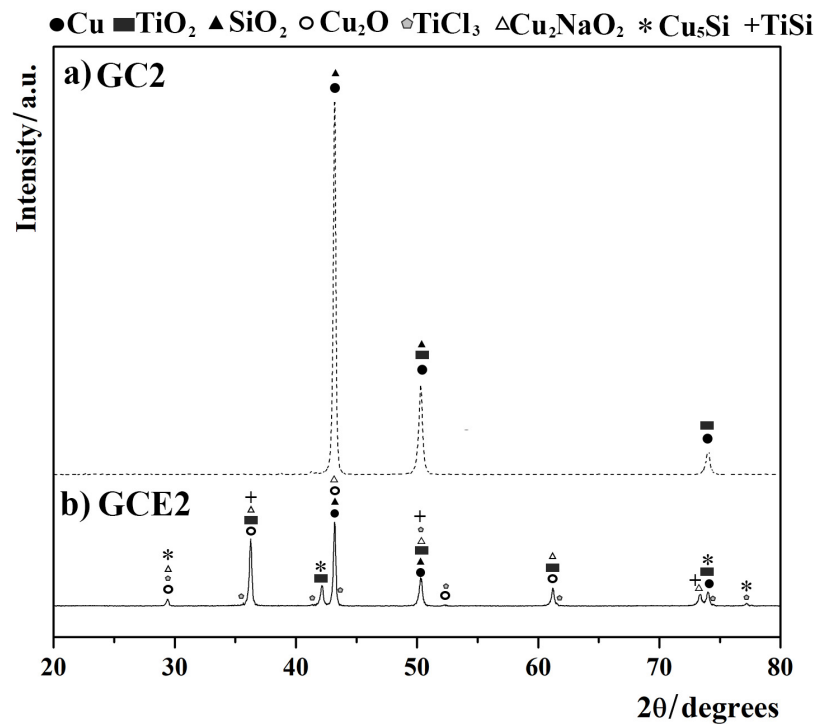
The preferential oxidation of silicon is attributable to the significant difference in free formation energy between  $\text{SiO}_2$  ( $-856.3 \text{ kJ mol}^{-1}$ ) and  $\text{Cu}_2\text{O}$  ( $-146 \text{ kJ mol}^{-1}$ ) under conditions of controlled oxidation, whether at room temperature or at  $100^\circ\text{C}$  [50].



**Figure 13:** Results of particle size analysis for precipitates in GCE2 and GCE3, featuring (a) and (d) standard normal distribution, (b) and (e) scanning electron micrograph, and (c) and (f) EDS spectrum.



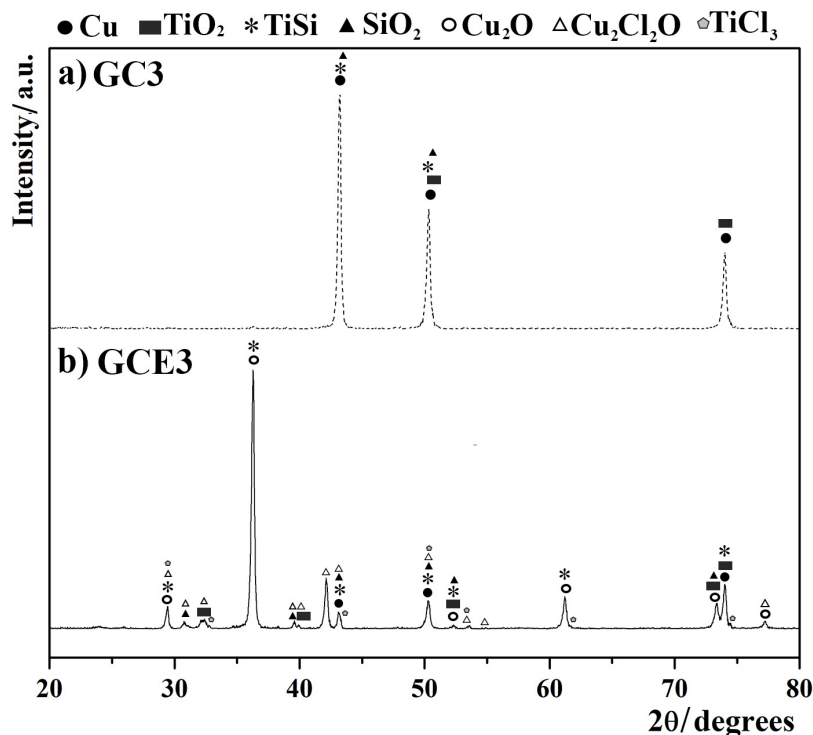
**Figure 14:** X-ray diffraction patterns of organic coating derived from GPTMS precursor: (a) GC1 and (b) GCE1.



**Figure 15:** X-ray diffraction patterns of organic-inorganic hybrid coating derived from GPTMS precursor +  $\text{TiO}_2$  particles: (a) GC2 and (b) GCE2.

In Figures 15a and 16a, the presence of crystalline phases Cu,  $\text{TiO}_2$ , and  $\text{SiO}_2$  in GC2 and GC3 is confirmed. The EDS analysis revealed the presence of Cl, O, and Na in G2 and G3, leading to the formation of compounds such as  $\text{Cu}_2\text{O}$ ,  $\text{CuNaO}_2$ , and  $\text{Cu}_5\text{Si}$ , which was confirmed by XRD (Figure 15b). The irregular distribution of  $\text{TiO}_2$  particles in GCE2 contributed to the growth of precipitates on the surface, like those seen in GCE1.

The presence of oxides in the coating, such as  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{Cl}_2\text{O}$ , resulted from reactions between the copper substrate and elements in the salt-spray, such as Cl and O (zone F in Figure 11c). In GCE3, the formation



**Figure 16:** X-ray diffraction patterns of organic-inorganic hybrid coating derived from GPTMS precursor + TTIP: (a) GC3 and (b) GCE3.

of titanium-silicon (TiSi) can be attributed to the reaction between titanium from the TTIP (titanium (IV) isopropoxide) and silicon from organosilane (Glycidopropyltrimethoxysilane), creating a dense and compact coating that enhanced the TiSi adhesive and other properties. It is important to note that TTIP performed better regarding surface roughness than the  $\text{TiO}_2$  particles [51]. GPTMS facilitated the deposition of TiSi and  $\text{SiO}_2$  through covalent chemical bonds, effectively anchoring them due to the proper surface finish ( $R_a = 0.197 \pm 0.3 \text{ } \mu\text{m}$ ) [52].

### 3.5. Evaluation of corrosion resistance using Electrochemical Impedance Spectroscopy (EIS)

The electrochemical response of the evaluated samples, as determined through potentiodynamic testing, is illustrated in Figure 17a. These curves display the corrosion potential, the corrosion current density, and the Tafel slopes for the cathodic and anodic branches of each curve [53]. These parameters were calculated according to ASTM G105 standards. The summarized results of this analysis are presented in Table 7. The results there indicate that the substrate (S1) has a corrosion potential of  $-590 \pm 0.1 \text{ mV}$  and a corrosion current density of  $2.398 \times 10^{-4} \pm 0.02 \text{ A}\cdot\text{cm}^{-2}$ . Applying the GPTMS+ $\text{TiO}_2$  coating (GC2) resulted in a significant shift in corrosion potential to a more cathodic value of  $-330 \pm 0.3 \text{ mV}$ , accompanied by a reduction in corrosion current density to  $1.38 \times 10^{-5} \pm 0.04 \text{ A}\cdot\text{cm}^{-2}$ . These results suggest that the GC2 coating offered improved corrosion protection compared to that of the uncoated substrate.

Similar results were observed with the GPTMS + TTIP coating (GC3), which exhibited a corrosion current density of  $1.047 \times 10^{-5} \pm 0.01 \text{ A}\cdot\text{cm}^{-2}$ , lower than the densities of the GC2 coating and the substrate (S1), which had values of  $4.86 \times 10^{-5} \pm 0.01 \text{ A}\cdot\text{cm}^{-2}$  and  $3.62 \times 10^{-5} \pm 0.02 \text{ A}\cdot\text{cm}^{-2}$ , respectively. Additionally, the GC3 coating showed a corrosion potential of  $-330 \pm 0.3 \text{ mV}$ , comparable to GC2, but with an even lower corrosion current density, indicating superior corrosion protection.

The results presented in Table 7 show that the substrate (S1) has a corrosion potential of  $-590 \pm 0.1 \text{ mV}$  and a corrosion current density of  $2.398 \times 10^{-4} \pm 0.02 \text{ A}\cdot\text{cm}^{-2}$ . The application of the GPTMS +  $\text{TiO}_2$  coating (GC2) resulted in a significant shift in the corrosion potential to a more cathodic value ( $-330 \pm 0.3 \text{ mV}$ ) and a reduction in the corrosion current density to  $1.38 \times 10^{-5} \pm 0.04 \text{ A}\cdot\text{cm}^{-2}$ . These results indicate that the GC2 coating provided improved corrosion protection compared to the uncoated substrate, by reducing the corrosion rate. Equivalent results were observed for the GPTMS+TTIP coating (GC3). This coating exhibited a corrosion current density of  $1.047 \times 10^{-5} \pm 0.01 \text{ A}\cdot\text{cm}^{-2}$  which is lower than densities of the GC2 coating and the substrate (S1), at  $4.86 \pm 0.01 \text{ A}\cdot\text{cm}^{-2}$  and  $3.62 \pm 0.02 \text{ A}\cdot\text{cm}^{-2}$ , respectively. Additionally, the GC3 coating showed a more positive corrosion potential ( $-330 \pm 0.3 \text{ mV}$ ), comparable to that of GC2, but with an even lower corrosion current density, indicating superior corrosion protection.

The Nyquist plots obtained for the substrate (S1), the hybrid organic-inorganic coating based on GPTMS combined with  $\text{TiO}_2$  particles (GC2), and the coating based on GPTMS with TTIP (GC3), in synthetic brine, are shown in Figure 17b. All the impedance spectra exhibit capacitive reactance. Notably, the charge transfer resistance, indicated as real impedance at the end of the Nyquist plot in the figure, increases for the coated samples compared to the substrate. The charge transfer resistance ( $R_{ct}$ ) for the substrate (S1) is approximately 918  $\Omega$ , while for the coated samples, it ranges from 6 to 1331  $\Omega$  for GC2 and from 6 to around 2764  $\Omega$  for GC3.

The data on charge transfer resistance reinforce the findings from the potentiodynamic tests, highlighting the superior effectiveness of the hybrid organic-inorganic coating based on GPTMS + TTIP (GC3), compared to both the substrate and the GPTMS coating combined with  $\text{TiO}_2$  particles (GC2). The GC3 coating demonstrated corrosion resistance ranging from 6 to approximately  $2764 \pm 10 \Omega$ , significantly outperforming the other coatings. This enhanced performance can be attributed to the formation of a denser and more coherent siloxane network resulting from the combination of GPTMS and TTIP. The observed mechanical interlocking provides greater cohesion and structural stability, forming a robust barrier against corrosive agents and minimizing defects that can be exploited by them.

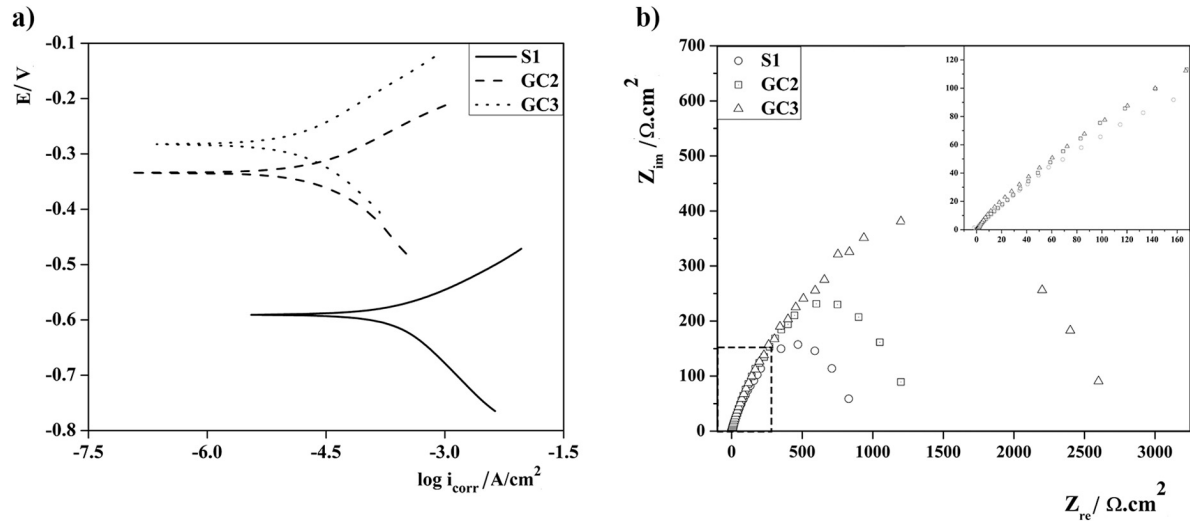
In contrast, the GPTMS +  $\text{TiO}_2$  (GC2) coating exhibited corrosion resistance ranging from 6 to around  $1331 \pm 6 \Omega$ , which is better than the substrate (S1) but lower than GC3. Despite improving corrosion protection, the GC2 coating suffered from surface cracking due to the stresses induced by the  $\text{TiO}_2$  particles' filling the coating's voids. These cracks allowed corrosive agents to penetrate, reducing the coating's effectiveness.

To calculate the corrosion rate,  $v_{corr}$ , using the provided  $i_{corr}$ , equation 1 was used [53]:

$$v_{corr} = \frac{K \times i_{corr} \times EW}{\rho}, \quad (1)$$

where  $K$  is a constant ( $3272 \text{ mm} \cdot \text{year}^{-1}$ , to obtain the corrosion rate in  $\text{mm year}^{-1}$ ),  $i_{corr}$  ( $\text{A} \cdot \text{cm}^{-2}$ ),  $EW$  is the equivalent weight of copper ( $31.75 \text{ g/equivalent}$ ), and  $\rho$  is the density of copper ( $8.96 \text{ g} \cdot \text{cm}^{-3}$ ).

Table 7 confirms that the substrate experiences significant corrosion at a rate of  $2.78 \text{ mm year}^{-1}$  ( $109.45 \text{ mpy}$ ), indicating high deterioration. In contrast, the corrosion rates for the coatings GC2 and GC3 are



**Figure 17:** (a) Polarization curves for substrate (S1), GPTMS +  $\text{TiO}_2$  coating (GC2), and GPTMS + TTIP coating (GC3), showing tafel slopes. (b) Nyquist plots for the samples: S1, GC2, and GC3 samples in synthetic brine.

**Table 7:** Results of polarization resistance analysis for the samples: substrate (S1), GPTMS +  $\text{TiO}_2$  coating (GC2), and GPTMS + TTIP coating (GC3) in synthetic brine.

| SAMPLE | $R_p/\Omega \cdot \text{cm}^{-2}$ | $i_{corr}/\text{A} \cdot \text{cm}^{-2}$ | $E_{corr}/\text{mV}$ | $v_{corr}/\text{mm} \cdot \text{year}^{-1}$ | IE  |
|--------|-----------------------------------|------------------------------------------|----------------------|---------------------------------------------|-----|
| S1     | $918 \pm 3$                       | $2.398 \times 10^{-4}$                   | $-590 \pm 0.1$       | 2.78                                        | *   |
| GC2    | $1331 \pm 6$                      | $1.38 \times 10^{-5}$                    | $-330 \pm 0.3$       | 0.16                                        | 94% |
| GC3    | $2764 \pm 10$                     | $1.047 \times 10^{-5}$                   | $-280 \pm 0.4$       | 0.12                                        | 95% |



much lower, at  $0.16 \text{ mm} \cdot \text{year}^{-1}$  (6.30 mpy) and  $0.12 \text{ mm} \cdot \text{year}^{-1}$  (4.72 mpy), respectively. This suggests that GC2 and GC3 offer superior corrosion protection compared to the substrate.

The corrosion inhibition efficiency of the coatings applied to copper (IE) was estimated using equation 2 [54]:

$$IE = \frac{i_{\text{corr},0} - i_{\text{corr}}}{i_{\text{corr},0}} \times 100 \quad (2)$$

where  $i_{\text{corr}}$  is the corrosion current density of the coating and  $i_{\text{corr},0}$  is the corrosion current density of the substrate. Based on this equation, the corrosion inhibition efficiency of the GC2 coating was 94%, while the GC3 coating demonstrated an efficiency of 95%. These values indicate that both coatings offer a significant improvement in corrosion protection compared to the uncoated substrate. However, the slightly higher efficiency of the GC3 coating suggests that the combination of GPTMS and TTIP provides an even more effective barrier against corrosion, making it the best-performing coating in this study. This slight difference in efficiency may reflect the greater integrity and cohesion of the siloxane network in the GC3 coating, contributing to more effective protection in corrosive environments [55].

#### 4. CONCLUSION

For the first time, results integrating profilometry, EIS, and inhibition efficiency (IE) in a salt-spray chamber highlight the superior performance of a hybrid coating based on GPTMS + TTIP (GC3), compared to other coatings and an uncoated substrate. During salt-spray exposure, SE1 developed a porous, less-dense crust that allowed corrosive agents to penetrate, accelerating corrosion and expanding the damaged area. Cracks and pores further concentrated mechanical stress, leading to localized corrosion and delamination between the coatings (GCE1, GCE2) and the S1 substrate.

However, GC3, a Class II hydrogel, demonstrated significantly enhanced adhesion to the substrate, due to mechanical interlocking, creating a protective barrier that slowed the corrosive process. This mechanism helped to form an intermediate layer of reaction products that interlocked with both the coating and the substrate, preventing precipitate growth and increasing resistance to corrosion.

Profilometry revealed a uniform reduction in the thickness of the GC3 coating by 66%, indicating controlled and homogeneous wear. The EIS results show that GC3 achieved a charge transfer resistance of up to  $2764 \pm 10 \Omega$ , compared to  $1331 \pm 6 \Omega$  for GC2 and  $918 \pm 3 \Omega$  for the substrate (S1), reinforcing the finding of GC3's superior barrier properties. The corrosion inhibition efficiency (IE) of GC3 was 95%, surpassing GC2's 94%, clearly demonstrating the advantages of the TTIP-based system. The presence of TTIP not only improved adhesion, but also maintained the coating's integrity, offering better corrosion resistance and surface quality than  $\text{TiO}_2$ -based coatings.

Unlike GC1 and GC2, which deteriorated significantly after salt-spray exposure, GC3 showed outstanding resistance, making it the most effective option for corrosive environments. Given its remarkable performance, future research could explore GC3's potential applications in photocatalytic and antibacterial fields, where its unique composition may offer additional benefits.

These results underscore the importance of selecting an appropriate coating to ensure durability and corrosion resistance in saline environments, with GC3 standing out as the optimal choice.

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