The influence of organophosphonic acid and conducting polymer on the adhesion and protection of epoxy coating on aluminium alloy

Viviane Dalmoro[a,b], Carlos Alemán[b,c], Carlos A. Ferreira,[d] João H. Z. dos Santos[a], Denise S. Azambuja[a,*], Elaine Armelin[b,c,*]

[a] Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500 - CEP 91501-970, Porto Alegre (RS), Brazil.

[b] Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, Avda. Diagonal 647, Barcelona E-08028, Spain.

[c] Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain.

[d] Departamento de Engenharia de Materiais, PPGEM, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Setor 4, Prédio 74- CEP 91501-970, Porto Alegre (RS), Brazil.

*Corresponding authors: elaine.armelin@upc.edu and denise@iq.ufrgs.br

ABSTRACT

In the present study we compared the beneficial effect on the incorporation of modified silane nanocoating and conducting polymer additive to the adhesion and protection of aluminium surface with epoxy coating. Results proved that the protection imparted by the silane coating, suitably modified with phosphonic groups, showed an excellent adhesion to the metallic substrate as well as good adherence with the epoxy outer layer, which result in an improved corrosion resistance. The incorporation of 1% of poly (3-methyl thiophene acetate) (P3TMA) also improved the adhesion force of the epoxy paint adhered to the aluminium surface. However, the adhesion force decreased with the increase of the immersion time in NaCl 3.5% solution. In conclusion, both bilayer systems [vinyltrimethoxysilane (VTMS)/tetraethylorthosilicate (TEOS) and VTMS/TEOS/ ethylenediaminetetra(methylene phosphonic acid) (EDTPO)] and also the employment of P3TMA in the epoxy coating showed better results in accelerated corrosion assays, *i.e.* very low blistering formation was observed, compared with control samples based in a monolayer coating directly adhered to the aluminium surface.

Keywords: sol-gel technology, epoxy coatings, silane compounds, conducting polymer, aluminium alloy

1. Introduction

The aluminium alloy 2024 properties, such as high strength-to-weight ratio, good fracture toughness and low cost, have maintained its dominant position in aerospace industry [1]. This kind of aluminium alloy has a complex distribution and composition of intermetallic particles. It is well known that corrosion process initiate in intermetallic particles, specifically in the S-phase with preferential dissolution of Al and Mg [2,3]. The localized corrosion constitutes the main degradation form of this alloy [2,4,5]. According to some authors the formation of stable pits evolves the cooperative mechanism, by galvanic coupling of intermetallic particles [6]. The cooperative corrosion process comprise the appearance and development of corrosion rings, whose intern surface act predominantly as a cathode and drives the anode into the surface, resulting in the grain boundary network. The grain boundaries attack evolves into an intergranular attack, leading to mechanical failure of this aluminium alloy [7].

One of the most important methods for corrosion protection is the employment of organic coatings, such as anticorrosive paints. A key feature in lifetime of organic coatings is its adhesion with the metal surface when exposed to corrosive medium [8], *i.e.*, the adhesion is one of the fundamental properties for a good corrosion protection. The physical-chemistry properties in the interface between metal and paint are usually improved by a pretreatment. The chromatization was a pretreatment widely used for light metals such as aluminium and its alloys, especially in the aerospace industry [9] due to its role as both anchoring for the organic coating and as corrosion inhibiting system. Nevertheless, the environmental restrictions have forbidden its utilization. In this context, the sol-gel process based on silica precursors are able to form bonds with both metal substrate and reactive groups of organic paint thought their functionalized organic group, due to silane bifunctionality [10]. Thus, as silane films assist the

interaction and adhesion with ensuing organic coating layer, they have been appointed as pretreatment or precoating for further paint deposition. Moreover, during the last years, attention has been given to the development of functional barrier coatings based on the modification of epoxy resins or polyurethanes with the incorporation of silanes or polyaniline molecules [11].

A wide amount of works concerning the anticorrosive performance of metals coated with sol-gel films obtained by silica precursors has been published [12-14]. Nevertheless, studies regarding the employment of sol-gel films as previous nanocoating layer for further paint deposition and metal protection are scarce. As an example, Bajat *et. al.* [15] has described the use of vynilsilane as a pretreatment of aluminium surface before epoxy paint deposition. On the other hand, Zand and Mahdavian [16] also reported the use of sol-gel films as previous coating for polyurethane paint deposition. They obtained good results of adhesion strength and corrosion protection.

The behavior of sol-gel films based on silica precursors as adhesion promoters and its anticorrosion action has been dependent on parameters such as, concentration of silane in the starting solution [15,17,18], silica precursor nature [17,18], pH of the starting solution [16,17], immersion time in the starting solution [15], nature of organic coatings [18] and the nature of the metal substrate [19].

Moreover, the silica precursor must be chosen so as to guarantee proper compatibility with the polymeric resin and to provide good interaction with the metal substrate. In our previous work we verified that the silica precursors, vinyltrimethoxysilane (VTMS)/tetraethylorthosilicate (TEOS), when mixed in adequate ratio (3/1) propitiate the suitable balance between hydrophobicity and porosity to be used as anticorrosive barrier and adhesion promoter [20]. We also verified that the

incorporation of a catalytic amount of phosphonic acid, ethylenediaminetetra(methylene phosphonic acid) (EDTPO), to silica network promoted the formation of Al-O-P bonds, resulting in a great benefit for silane adhesion and corrosion protection [21-25].

Therefore, the main aim of the present work is combine the anticorrosive and adhesion properties propitiated by VTMS/TEOS nanocoating covalently bonded to the aluminium surface with a well-known anticorrosive epoxy primer, forming a bilayer system for the protection of AA2024 aluminium alloy. In order to improve the previous results with AA2024 alloy, two further approaches were investigated: (i) the incorporation of EDTPO to the VTMS/TEOS sol-gel formulation and (ii) the incorporation of a conducting polymer to the epoxy paint. Since the advantage combination of the use of conducting polymers (CPs), as anticorrosive additive, with organic coatings has granted the improvement of corrosion protection of metals [26-30], accordingly, we incorporated a soluble semiconducting polythiophene derivative (P3TMA) to the epoxy paint formulation in order to evaluate its influence to the adhesion between the sol-gel inner nanocoating and the epoxy outer coating.

2. Experimental

2.1 Preparation of AA2024 substrate and sol-gel films deposition

AA2024-T3 rectangular samples 5 x 10 cm were prepared by grinding with silicon carbide papers up to 1200 grit. For the aluminium alloy treated with silica precursors, the samples was firstly immersed in a 0.05 mol L^{-1} acetic acid solution for 5 min and washed with distilled water and dried under a hot air stream [23]. Then, the panels were immersed in the starting solutions of silica precursors for 30 minutes, followed by dry in an oven at 110°C during 1 h for curing. The starting solutions consist of 50 % (v/v) ethanol (Nuclear, 99.5 %), 46% (v/v) deionized water (18.3 MΩ cm), 1%

(v/v) TEOS (Merck, 98 %) and 3 % (v/v) VTMS (Aldrich, 97 %), which were mixed for 1h and stored for 3 days prior use. The phosphonic acid EDTPO (Dojindo, Japan, 97%) was added to this starting solution with molar concentration of 3.75×10^{-5} mol L^{-1}. The resulting films were denoted as 3V and 3VE5 for sol-gel without and with phosphonic acid, respectively.

The thicknesses of the as-prepared 3V and 3VE5 films were measured with a profilometer Dektack Veeco 150. The sol-gel films thickness varied from 190-200 nm, respectively, without and with phosphonic acid adhesion promoter.

2.2 Paint application

The primer applied after the sol-gel films deposited onto AA2024 surface is composed by two components epoxy-polyamide material commercialized by Industrias Titan S.A. (Epoxy bicomponent Titan 831). The resin-hardener ratio (v/v) used was 4/1 according to the manufacturer recommendations. The mixture was prepared at room temperature by stirring for about 20 minutes before metal painting. The samples coated with sol-gel film were immersed into the reservoir containing the liquid paint. The painted specimens were allowed to cure for 7 days at room temperature. The conducting polymer, poly (3-methyl thiophene acetate) (P3TMA), was synthesized following the procedure described by Kim *et al.* [31] and was incorporated into commercial epoxy paint in the concentration of 1% wt. dispersed in chloroform solvent. Before addition, the CP powder was sonicated carefully and filtrated to eliminate any insoluble particle, and it was vigorously stirred to good homogenization in the liquid paint.

Once the paint was completely dried, thickness was measured by using an electrometer Mega-Check Pocket (Neurtek S.A.) The apparatus was previously calibrated to non-ferrous substrate by using the gauges supplied. The epoxy coating

thickness varied from 70 to 80 μm, in agreement with the thickness estimated by cross-section SEM images (Figure 1).

2.3 Measurements

2.3.1. Infrared spectroscopy (FTIR)

The composition of the solid films, either sol-gel films or organic coatings, was monitored by FTIR spectroscopy. Structural characterization of the cured silane nanocoating, covalently bonded onto aluminium surface, was performed using a Nicolet 6700 FTIR spectrometer equipped with Smart SAGA (specular aperture grazing angle, with an incidence angle of 80º from the normal surface) accessory, whereas the epoxy coating was examined using an ATR-Smart Orbit accessory. All spectra were recorded in a wavenumber range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}.

2.3.2. X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed in a SPECS system equipped with a high-intensity twin-anode X-ray source XR50 of Mg/Al (1253 eV and 1487 eV, respectively) operating at 150 W, placed perpendicular to the analyzer axis, and using a Phoibos 150 MCD-9 XP detector. The X-ray spot size was 650 μm. The pass energy was set to 25 and 0.1 eV for the survey and the narrow scans, respectively. For the flood gun, the energy and the emission current were 0 eV and 0.1 mA, respectively. Spectra were recorded with a pass energy of 25 eV in 0.1 eV steps at a pressure below 6×10^{-9} mbar. The C1s peak was used as an internal reference with a binding energy of 284.8 eV.

2.3.3. Scanning electron microscopy (SEM)

SEM analyses were carried out using a focused-ion-beam Zeiss Neon 40 scanning electron microscope equipped with an energy-dispersive X-ray (EDX)

spectroscopy system and operating at 5 kV. Samples were mounted on a double-sided adhesive carbon disc and sputter-coated with a thin layer of carbon to prevent sample charging problems. For cross-section SEM images, samples were polished until mirror surface with an automatic polishing machine Presi Mecapol 230.

2.3.4. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was performed as a function of time, in 3.5 wt. % NaCl solution and at open circuit potential (OCP). Three systems were considered: (i) bare alloy, (ii) alloy coated with sol-gel films (with and without phosphonic acid) and (iii) alloy coated with epoxy coatings (iv) alloy coated with sol-gel and epoxy coatings (with and without conducting polymer). A three-electrode electrochemical cell arrangement was used, consisting of the AA2024-T3 panel with 0,785 cm^2 of exposed area (working electrode), Ag|AgCl saturated electrode (reference electrode), to which all the potentials were referred, and a Pt mesh (counter electrode). The electrochemical measurements were performed using an AUTOLAB PGSTAT302N (Ecochimie, The Netherlands) equipment. The amplitude of the EIS perturbation signal was 10 mV, the frequency ranged from 10^5 to 10^{-2} Hz taking 7 frequencies per decade.

2.3.5. Accelerated Corrosion Tests

Accelerated corrosion tests were performed using an home-made equipment patented in our laboratory and previously reported [32,33]. In this equipment the painted metallic samples are placed in a support, which is controlled by a programmable device. The robotized equipment allows immersion, dropping, drying and cooling processes, which are distributed in programmed cycles. The typical operating conditions for one cycle are: (a) immersion of the painted aluminium alloy pieces into the solution (15 min); (b) wringing of the aluminium alloy pieces (15 min); (c) drying forced with

bulbs (230 V-100W, 15 min); and (d) cooling at room temperature (15 min). Thus, every cycle takes 60 min. The total number of cycles were 1440, corresponding to 60 days of samples exposure in NaCl 3.5 wt.% medium. The coated panels were scribed before the accelerated corrosion tests and the corrosion progress was evaluated according to ASTM D1654 [34] (Standard Test Method for Evaluation of Painted or Coated Specimens) and cross-sectional SEM images.

2.3.6. Adhesion tests

The adhesion strength of coatings on AA2024 discs was determined by pull-off test, according to UNE-EN-ISO 4624 [35], using KN-10 (Neurtek S.A.) adhesion equipment. For dry adhesion substrates the painted panels and dolly, 20 mm in diameter, were bonded using a two-component epoxy adhesive. After 24 h of cure, a slot around the dolly until reached the substrate was done to avoid the effect of peripheral coatings. For each system, two panels and three areas were examined and those with the interfacial failure were considered and the minimum force to detach the coatings from substrate was recorded accordingly. For wet adhesion, procedure was the same; however the substrates were previously subjected to accelerated corrosion assays using the robotized equipment described on previous section.

3. Results and Discussion

3.1 Characterization of silane and epoxy primer coatings

FTIR spectra were recorded for sol-gel nanolayer and epoxy primer films. The main absorption bands are showed on the Figure 2. As it can be seen, the main absorption bands from sol-gel film correspond to the OH bands from silanol groups (3500-3200 cm^{-1}, 890 cm^{-1}), Si–O–Si linkages (779, 1076 and 1172 cm^{-1}) [36-38] and C=C bonds (1600 cm^{-1}) from VTMS monomer [38], the latter being overlapped with P–

O-Al stretching absorptions (Figure 2a). Network formation can also been checked by the presence of cyclic Si–O skeletal bands appeared at about 548 cm^{-1} and 463 cm^{-1}. Accordingly, the FTIR spectrum confirms the cross-linked structure of the hybrid silane coating.

Figure 2b shows the main absorption bands of the cured epoxy-polyamide primer. Broad band occurs in the range of 3500–3200 cm^{-1} due to the presence of both O-H and N-H stretching vibrations. Furthermore, the presence of strong bands in the 1246 cm^{-1} region was identified as ArC–O–C–alkyl (ether group) from bisphenol A. On the other hand, the broad absorption band observed at around 1000 cm^{-1} corresponds to silicates (Si-O) usually employed as pigments in paint formulations. Other relevant bands are: C-H stretching (2964, 2927 and 2873 cm^{-1}), aromatic C=C (1607 cm^{-1}), C-H of methyl and methylene groups (1461 and 1508 cm^{-1}), a doublet of the *gem*-dimethyl groups from bisphenol A (~1380 cm^{-1}), aromatic ether (1244 cm^{-1}), and C-H out-of-plane bending from *p*-substituted benzene (829 cm^{-1}). The absence of the absorption band of epoxy ring terminal group (~915 cm^{-1}) and the presence of OH and NH groups corroborate to check that the curing process has been completed. As expected, the addition of a small concentration of CP to the coating formulation is not appreciable by FTIR spectroscopy, which was already described in our previous studies [39].

XPS was also performed to bare alloy and AA2024-T3 coated with sol-gel films 3V and 3VE5 (Figure 3). As expected, the survey spectrum of AA2024 shows the presence of mainly aluminium and oxygen elements but also low concentrations of Cu, Mn and Fe metals. The nitrogen and carbon detected are due to the adsorption of air during the ambient exposition. On the other hand, the XPS spectra of the substrate coated with 3V and 3VE5 films evidence the presence of silicon, carbon and oxygen. The aluminium peak heights detected for the 3V and 3VE5 samples are significantly

lower than that of the AA2024, which is consistent with the film formation onto metallic surface. However, phosphorous was not detected at the silica surface in the 3VE5 network composition. According to our previous study [20], P 2p binding energy can be detected only after forty minutes of depth profiling, proving the hypothesis that organophosphonic groups actuate by formation of Al-O-P bonds, which promote a more compact layer in the interface metal/sol-gel film. The main binding energy of elements from silane coating and alloying metals from bare metal has been showed in the Figure 3.

3.2 EIS measurements in 3.5% of NaCl aqueous solution

EIS analyses were carried out to evaluate the corrosion protection of the aluminium surface employing a coating barrier. The total immersion time in NaCl solution varied from 7 days to 10 months, if the barrier protection were the panels coated with the sol-gel nanocoating or the bilayer coating composed by sol-gel film and epoxy primer, respectively. In the first case, after 24h of immersion (Figure 4a) the beneficial action of sol-gel films is evident, if compared to the bare alloy. Both sol-gel films, without (3V) and with EDTPO (3VE5) presents higher phase angle and log |Z| than the uncoated metal surface. This behaviour is attributed to silica barrier network and to the interface between silica and metal composed by metalosiloxane covalent bonds and oxide layer, being detected as two relaxation process at high and medium frequency [13,29,21,24], respectively (Figure 4a). Nevertheless, the protective response of 3V and 3VE5 films decreases after 7 days of exposition to 3.5 % NaCl (Figure 4b). Thus, an additional coating is necessary for effective protection of aluminium surface if long immersion time is required.

In this way, the electrochemical response for samples coated with the sol-gel/epoxy system is completely different from those samples coated with a sol-gel film,

even after 30 days of immersion in extremely hard corrosive medium. As we can see, in the Figure 5a, the phase angle is close to 90 degrees for all samples, coated or uncoated with bilayer films, which means that the epoxy film is actuating as a barrier layer during this period.

However, with the progress of time (Figure 5b-d), significant differences appear when comparing samples which incorporates sol-gel/epoxy coatings than samples covered with a single layer of epoxy primer. The Bode diagrams for 3V/epoxy, 3VE5/epoxy and 3V/epoxy-P3TMA system are characterized by a relaxation process in a broad range of frequencies on all evaluated times, whereas samples without sol-gel film present from 300 days at least two relaxation processes. Therefore, in the panels treated with sol-gel nanocoatings as intermediate layer, we only appreciate one time constant due to a high resistance to corrosive species diffusion across the coating film, *i.e.*, it not possible detected separately the relaxation process of sol-gel film. This result is in agreement with some works that evaluated the sol-gel films deposited as pretreatment for organic coatings depositions [15,18,40,41]. In these works the thickness of organic coating layer varied from 40 to 140 μm. Therefore, the high thickness of our epoxy coating (75-80 μm) is also responsible by the detection of only one relaxation process in a broad frequency range. Thus, the wide observed relaxation process is associated mainly to organic coating pore resistance, which represents the extent of ionic conduction through the polymer layer in the immersion solution and capacitance of intact film [42,43].

The coating resistance achieved was about $10^{9.5}$ Ω cm^2 for all alloy substrate coated with sol-gel films and epoxy primer and remain constant up to 300 days. For aluminium alloy coated with epoxy coating, without sol-gel film, the impedance profile is similar that panels protected with the bilayer system (sol-gel/epoxy coating).

However the overall impedance value decreases after 160 days of immersion in NaCl solution achieving $10^{8.9}\,\Omega$ cm^2. Increasing the immersion time it should be noted that the total impedance modulus decreases from $10^{8.5}\,\Omega$ cm^2 to $10^{7.9}\,\Omega$ cm^2 after 220 and 300 days, respectively. In the longer assessed time at least three relaxation processes are detected. In this immersion time of aggressive agents, water, oxygen and chloride ions, penetrate through epoxy coating and reach the aluminium alloy surface resulting in the fall of impedance modulus, which doesn't occur with sample pretreated with sol-gel nanocoatings.

Regarding the differences between the two pretreatments, *i.e.* with 3V and 3VE5, it was more difficult to ascertain due to the excellent barrier properties of the epoxy paint, as evidenced from EIS analysis. However, the obtained results prove the beneficial action of VTMS/TEOS and VTMS/TEOS/EDTPO films as adhesion promoters and as anticorrosive system compared to the samples without sol-gel-films.

3.3 Cyclic accelerated corrosion assays in 3.5% of NaCl aqueous solution

In order to evaluate the anticorrosive performance, accelerated assays were performed using an automatized system for panel immersions in NaCl solution. In the Figures 6 we compare the panel photographs taken after 7, 30 and 60 days of accelerated corrosion experiments for AA2024 coated with epoxy (without sol-gel films) and coated with different sol-gel precoatings and epoxy primer.

Loss of adherence from epoxy paint without pretreatment (AA2024/epoxy) appear after only 7 days of cyclic immersion in NaCl solution (Figure 6a). However the delaminated area around the scribe is very small, being observable localized corrosion in this area with optical microscope (Figure 6a, inset). As increasing the exposure time

to 15-30 days, the delaminated area grows significantly and after 60 days (Figure 6i) the corrosion is very intense for panel without sol-gel pre-treatment.

As a result of the electrolyte penetration in the epoxy paint without sol-gel inner film, the delamination occurs before safe protection time. Thus, the AA2024 surface is exposed to the aggressive medium. Regarding the corrosion products observed, the red coloration is due to the deposition of copper on the metallic surface, which is consistent with the proposed corrosion mechanism of AA2024 corrosion [2,3]. A porous structure of copper resultant by the preferential dissolution of Al and Mg of Al_2MgCu intermetallic is formed. In order to reduce the surface energy, small metallic Cu clusters are detached from porous structure [2,3]. The movement of the solid solution associated to incorporation of Cu clusters in hydrous oxide corrosion product allows the Cu redistribution in the outside region of the intermetallic particle, leading to propagation of the corrosion phenomenon.

On the other hand, it is worth noting that the corrosion rate is quite slow for the other three systems pretreated by sol-gel films (3V/epoxy, 3VE5/epoxy and 3V/epoxy-P3TMA) in the same period of immersion time. As can be seen in the Figure 6, the presence of increasing blistering size, due to the penetration of the electrolyte under the paint, like that occurred in the AA2024/epoxy panels, were not observed for samples protected with sol-gel precoating. For panels protected with sol-gel films the delamination occurs at some localized points around the scribe after 60 days of exposure time assayed, proving that the electrolyte cannot penetrate under the coating due to the strong adherence promoted between aluminium surface-silane-epoxy coatings.

The evolution of the failure area under the film vs. time, according to the ASTM D-1654, is shown in Figure 7. As it was expected, the percentage of the failure area for

the aluminium alloy without sol-gel films intensifies quickly with the increase time of accelerated corrosion assays (Figure 7, inset). The percentage of corroded area for the untreated panel increased almost four times from 15 days to 30 days (7.8 % and 29.3%, respectively), and continues growing after 60 days of immersion (32%). For the systems precoated with sol-gel films the failure area is not appreciable until 60 days of immersion time and is also very slow, varying from 0.8% to 1.3%, evidencing the beneficial effects of sol-gel films and also the incorporation of conducting polymer as adhesion promoters.

The cross-section SEM analyses revealed that corrosion effect was important for panels not treated with sol-gel films. As we can see in the Figure 8a, after 30 days, the epoxy coating is completely delaminated and the corrosion of the alloy in some regions reaches a depth of 20 μm. Another observation is that the corrosion products are distributed in surface and below them there is an intensive corrosion process, being detected intergranular corrosion, as reported by Hughes *et al.* in previous studies for the AA2024-T3 [6]. On the other hand, panels protected with sol-gel film composed by TEOS-VTMS (Figures 8b) only present corrosion around the scribe. The SEM images corroborate with the preliminary accelerated corrosion results, the bilayer coating is well adhered because the coating does not delaminate after full immersion time in NaCl.

EDX analyses were taken on different zones of the AA2024 panel surface coated with 3V/epoxy system in order to determine the nature of the corrosion products (Figure 8b). EDX spectrum of point 1 (Figure 8c) revealed the presence of aluminium, oxygen and chlorine ions, probably corresponding to typically $Al(OH)_2Cl$ and $Al(OH)Cl_2$ corrosion products reported elsewhere [12], and also due to the high size of the corrosion particles (also observed under the organic film). EDX spectrum of point 2 (Figure 8d) corresponds mainly to aluminium alloy composition, with high

concentrations of Al and Cu. At point 3 (Figure 8e), it was firstly attributed to a pitting corrosion however EDX analysis revealed the presence of Si, C and O elements corresponding to the sol-gel coating (TEOS-VTMS), also it reveals an important concentration of Al from the metal substrate and, finally, high concentration of Cl element from probably the corrosion products close to this zone.

We can distinguish the different alloying elements and corrosion products with a SEM compositional mapping (Figure 9). The small whitish spots in SEM image correspond to intermetallic particles enriched in Cu, Mg, Mn and Fe. Two types of intermetallic particles were detected: Al-Cu-Mg and Al-Cu-Mn-Fe. High Cl ion concentration occurs in regions where the oxygen dominates, evidencing the formation of corrosion products, as described in 3V/epoxy system (Figure 8c).

We have to point out that the differences regarding the employment of phosphonic acid (EDTPO in 3VE5 samples) or conducting polymer (P3TMA in 3V/epoxy-P3TMA samples) in the failure area test (ASTM D1654, Figure 7) proves that both improve the adherence between interfaces metal-silane and silane-epoxy coating, respectively. However, relevant differences in the cross-sectional SEM analysis were not detected.

3.4 Adhesion measurements

Since the adhesion is a primordial requirement for achievement good mechanical and physical chemistry properties in the coated metal surface [17], the adhesion of the monolayer and bilayer paints was evaluated by pull-off tests (UNE-EN-ISO 4624). Pull-off measurements were carried before and after different time of accelerated assays (Figure 10).

The failure mode was adhesive for all samples, *i.e.*, it occurred in the interface between epoxy paint and adhesive layer. The samples with sol-gel films present higher adhesion strength than samples uncoated with silane. Therefore, as was evidenced in the previous section, the former will have better corrosion protection than the later.

Generally, the adhesion decreases with the increase of immersion time of the samples in the electrolyte. Additionally, the adhesion reduction was calculated considering the dry sample and the immersion time of 60 days. Surprisingly, the adhesion reduction was 0% for the system that contains organophosphonic molecules (3VE5/epoxy). It is only possible if these molecules are actuating as an adhesion promoter [19-24]. Thus, phosphonic acid has a positive effect on the adhesion of silane coating to the aluminium surface. The effect of the addition of P3TMA (1%) in the paint formulation was also noticed by pull-off test (Figure 10). The tensile strength obtained for samples in dry state is much higher than the sample with 3V nanocoating, corroborating to the idea that conducting polymers also can actuate as adhesion promoters [26-30]. However, this effect was lost over time in the wet samples, where the adhesion reduction was almost the same than panels coated with 3V/epoxy bilayer system (15% and 16.7%, respectively).

The panels directly coated with epoxy paint presents an adhesion reduction of 40% after 60 days. Therefore, the obtained results reveal that sol-gel precoatings propitiate an improvement of the adhesion of epoxy paint on the AA2024 surface. Further, these adhesion results indicate that the silane systems chosen (VTMS/TEOS or VTMS/TEOS/EDTPO) are also well adhered to the epoxy paint, because cohesive failure between the silane and epoxy coating was not observed. Other works also emphasize the beneficial synergy between silane compounds and organic coatings. Using EDX analysis, Seré *et al.* [44] concluded that the adhesion failure occurred in the

interface silane/zinc for hot dip galvanized steel pretreated with γ-mercaptopropyltrimethoxysilane and coated with polyurethane paint. Concerning the interface silane/organic coating, good adhesion was obtained.

Besides of adhesion on interface sol-gel film/organic coating, the precoating films are formed by a network composed by Si-O-Me and Si-O-Si linkages that offer an additional barrier to penetration of water and electrolytes on metal surface, contributing to a better response against corrosion. According to Mohseni *et al.* [17] the sol-gel pretreatment increases the surface free energy, leading to the improvement of wettability of substrate, and consequently, greater adhesion properties.

To conclude, both sol-gel films 3V and 3VE5, gives excellent adherence between the metal surface and the epoxy coating. The employment of conducting polymer to the paint formulation also gives excellent adherence and corrosion protection to AA2024 surface, according to our results from accelerated corrosion assays and pull-off test. Meanwhile, it shows a small difference between 3V/epoxy and 3V/epoxy-P3TMA systems, suggesting that 1% of conducting polymer is not enough to maintain the adhesion over time of immersion, in comparison to the incorporation of phosphonic acid to the silane coating (3VE5/epoxy). Therefore, more investigation concerning the role of conducting polymer as adhesion promoter between the epoxy and silane coatings need to be performed in the future.

4. Conclusions

One of the most important conclusion from this study is that the silane coating (VTMS/TEOS), suitably modified with phosphonic groups (EDTPO), shows excellent adhesion to metallic substrate as well as good adherence with the epoxy outer layer,

which results in an improved corrosion resistance. On the other hand, the characterization of an ultra-thin and transparent film is a difficult task. The characterization of the silane nanocoating was only possible using a grazing incidence FTIR analysis, which allows the study of ultra-thin films (from 10 Å to 0.5 μm) deposited on metallic substrates. Furthermore, XPS technique allows prove that the network sol-gel films are homogenously distributed on the aluminium alloy surface. Peaks from Al2p binding energy were not detected after the silane curing process.

Accelerated corrosion assays showed better results with the employment of bilayer systems (sol-gel and epoxy), which was evidenced by the lower blistering compared with control samples based in monolayer system (AA2024/epoxy). The EIS data indicated that the sol-gel/epoxy coating is more effective in the corrosion protection in agreement with accelerated corrosion experiments. Nevertheless differences in the system containing or not phosphonic acid were not detected.

The presence of a very thin layer of silane coating is essential for the good adherence of the epoxy primer, and also acts as a barrier coating to the penetration of chloride ions avoiding. Therefore, the pitting phenomenon under the coating and its delamination were not observed. The presence of 1% of conducting polymer (3V/epoxy-P3TMA) seems to be not essential for the film protection if compared with the film with silane (3V and 3VE5). However, it showed higher adhesion force compared to the other three systems, including the sol-gel system modified with phosphonic acid.

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Figure Captions

Figure 1. Cross section scanning electron microscopy of epoxy paint deposited onto AA2024-T3.

Figure 2. (a) FTIR-SAGA spectra of the cured silane nanocoating (3VE5), employed as inner coating, and (b) FTIR-ATR spectra of the epoxy film, used as topcoat.

Figure 3. Comparison of the XPS spectra of bare alloy and aluminium alloy coated with the 3V and 3VE5 films after 10 min of sputter depth profiling.

Figure 4. Bode diagrams of AA2024 bare alloy and AA2024 substrate coated with 3V and 3VE5 sol-gel precoatings after (a) one day and (b) 7 days of immersion in 3.5 % NaCl solution.

Figure 5. Bode diagrams obtained for the sol-gel/epoxy coating bilayer systems after (a) 40 days, (b) 160 days, (c) 200 days and (d) 300 days of immersion in 3.5 % NaCl solution.

Figure 6. Photographs of AA2024 panels coated with epoxy paint without silane precoating (a-b-c), precoated with 3V (d-e-f), precoated with 3VE5 (g-h-i), and precoated with 3V and P3TMA incorporated to the epoxy paint (j-k-l) after 7, 15 and 30 days of accelerated corrosion tests.

Figure 7. Percentage of corroded area of the AA2024 surface coated with epoxy paint (inset) and different silane precoating after accelerated corrosion assays in NaCl 3.5%.

Figure 8. SEM micrography of a cross section of AA22024 coated with: (a) the epoxy primer without silane nanocoating as intermediate layer, (b) precoated with 3V (TEOS-VTMS), (c-d-e) EDX analysis for the points 1-3 indicated in (b). Samples analysed correspond to an immersion time of 30 days.

Figure 9. SEM compositional mapping images for AA2024 coated with epoxy paint and after 30 days of accelerated corrosion assays.

Figure 10. Adhesion strength of AA2024 panels coated with epoxy and sol-gel films before and after accelerated corrosion assays in 3.5 wt. % of NaCl solution.
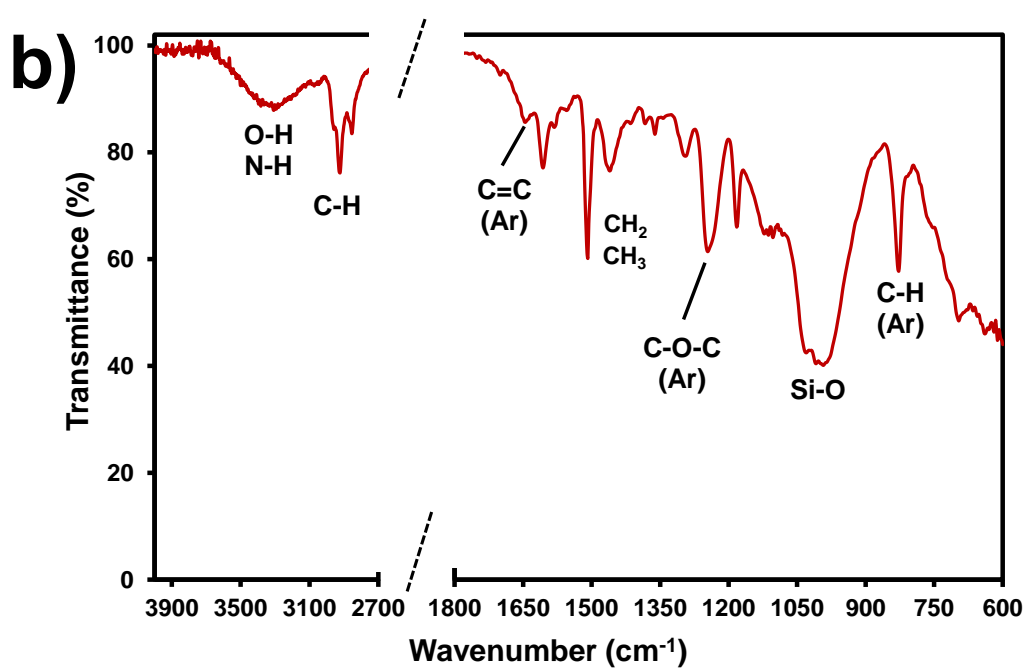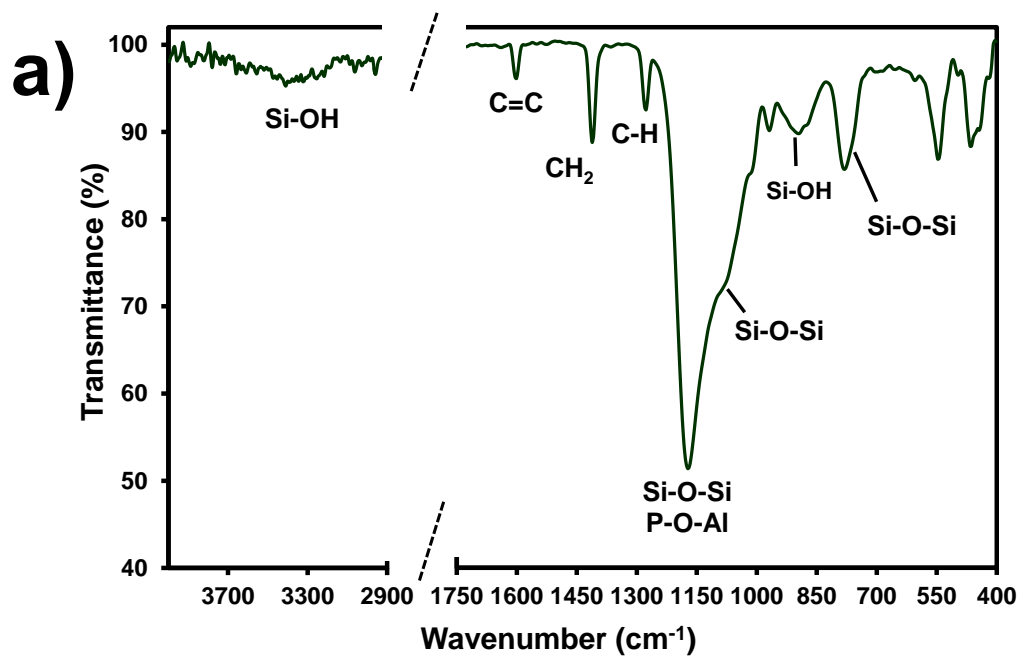
76.9 μm

30 μm
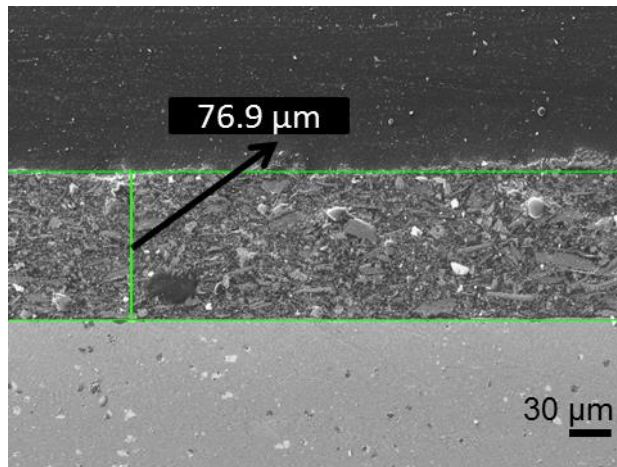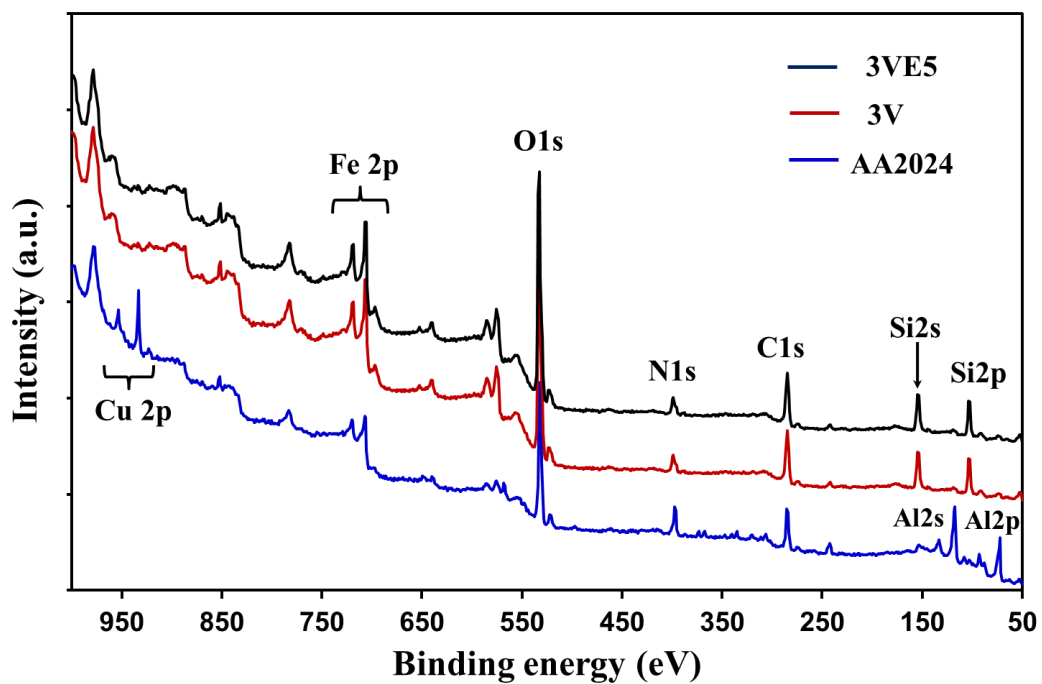
Figure 1

Figure 2

Figure 3
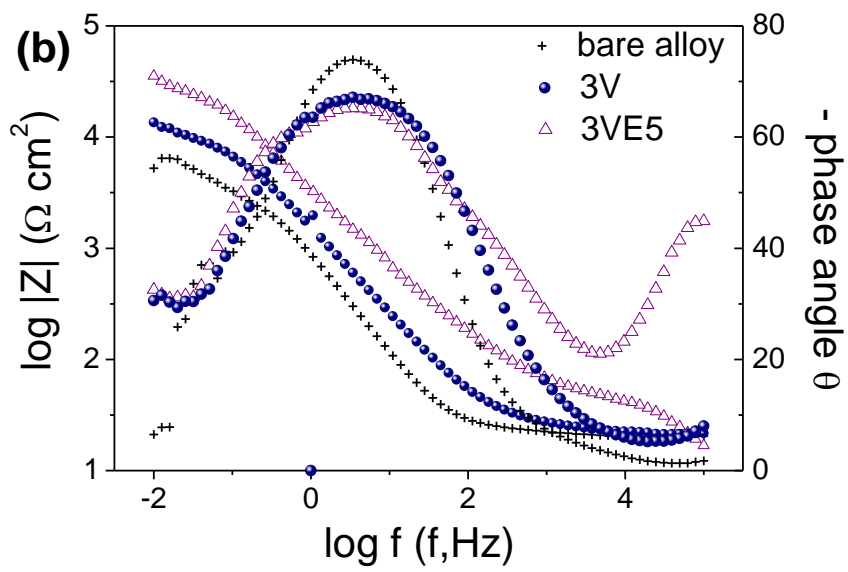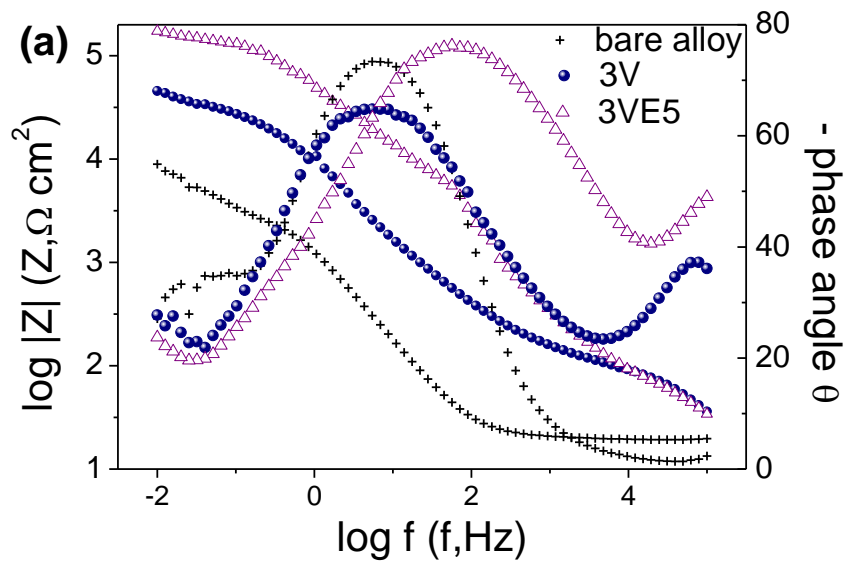
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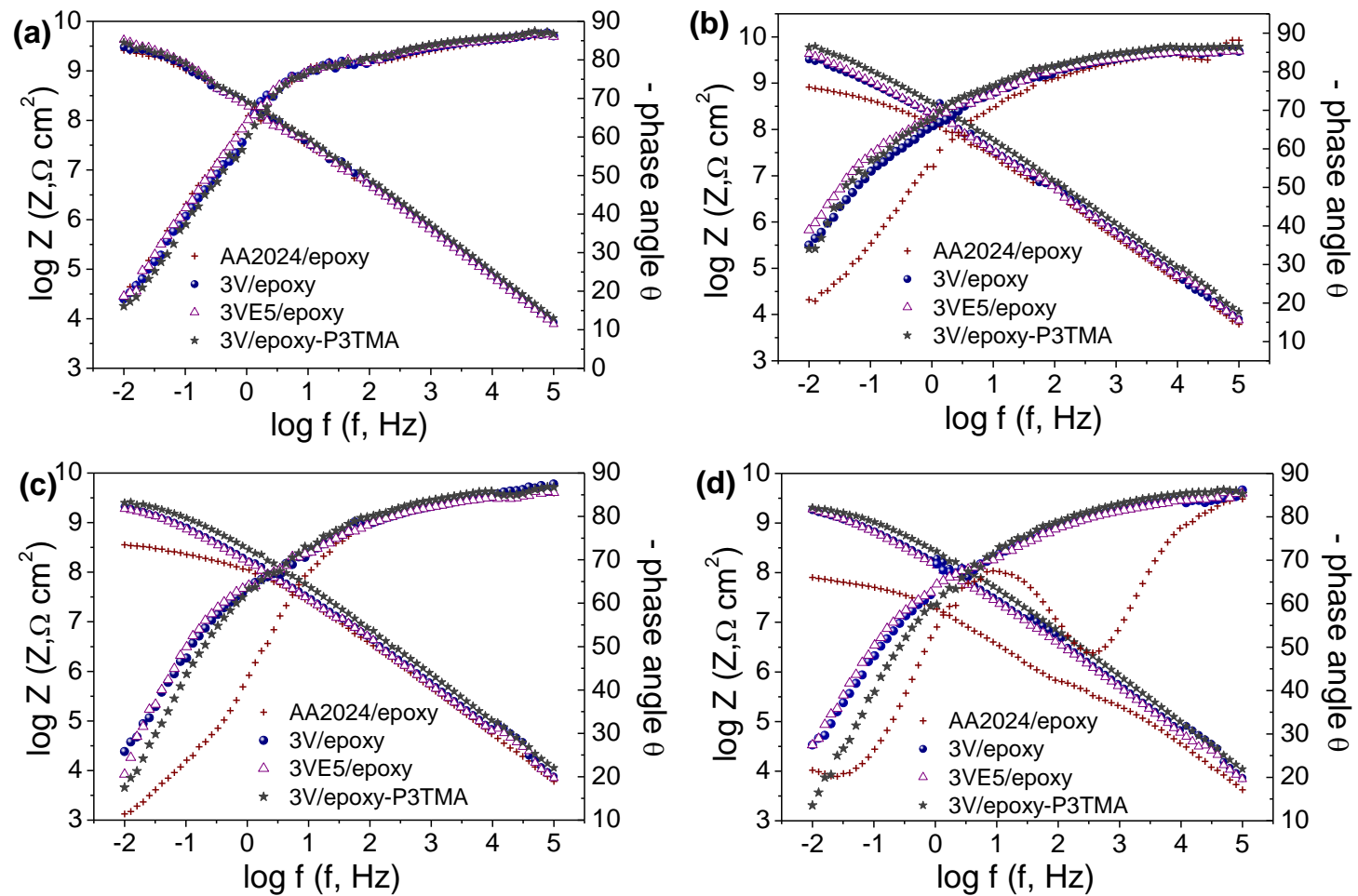
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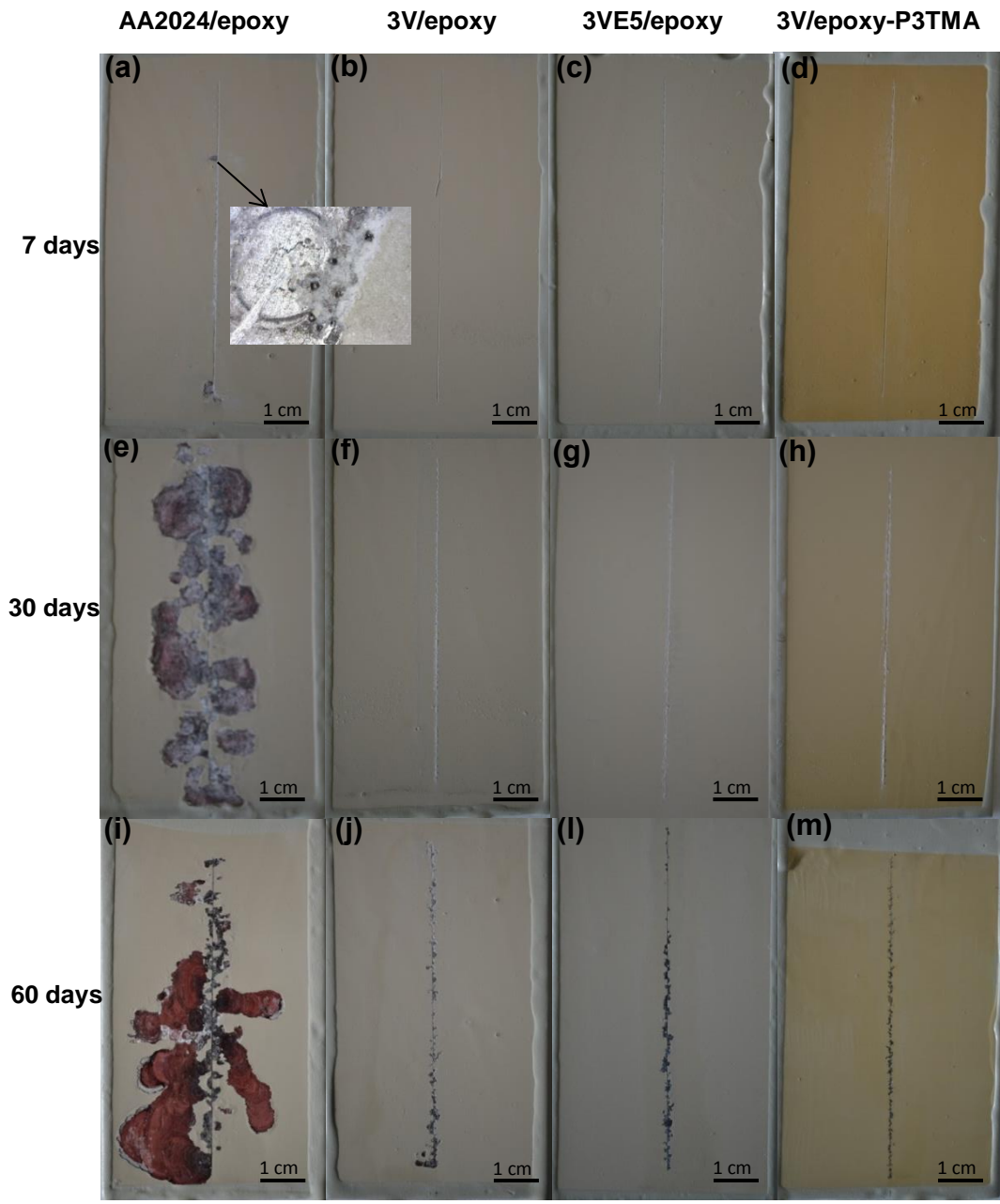
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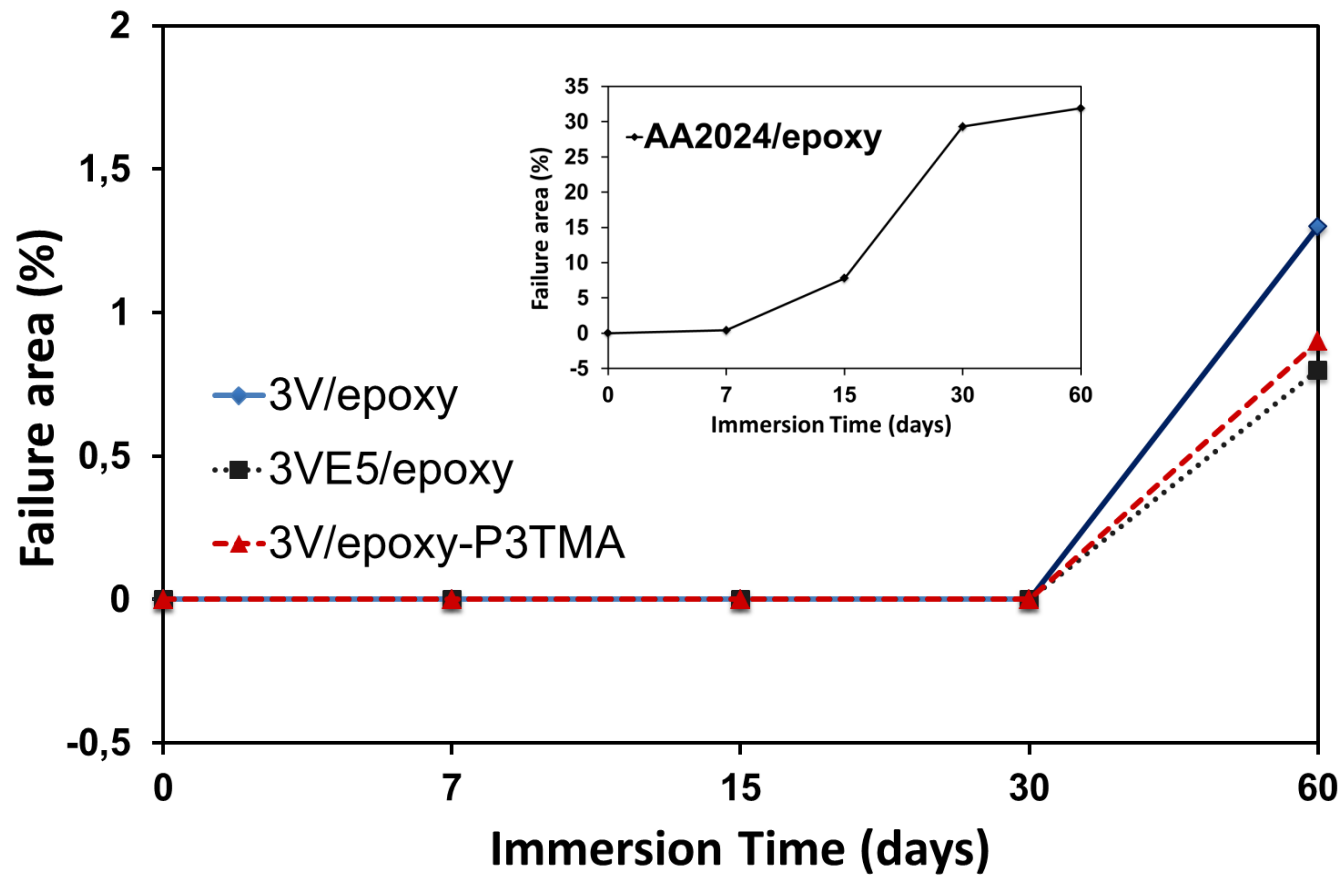
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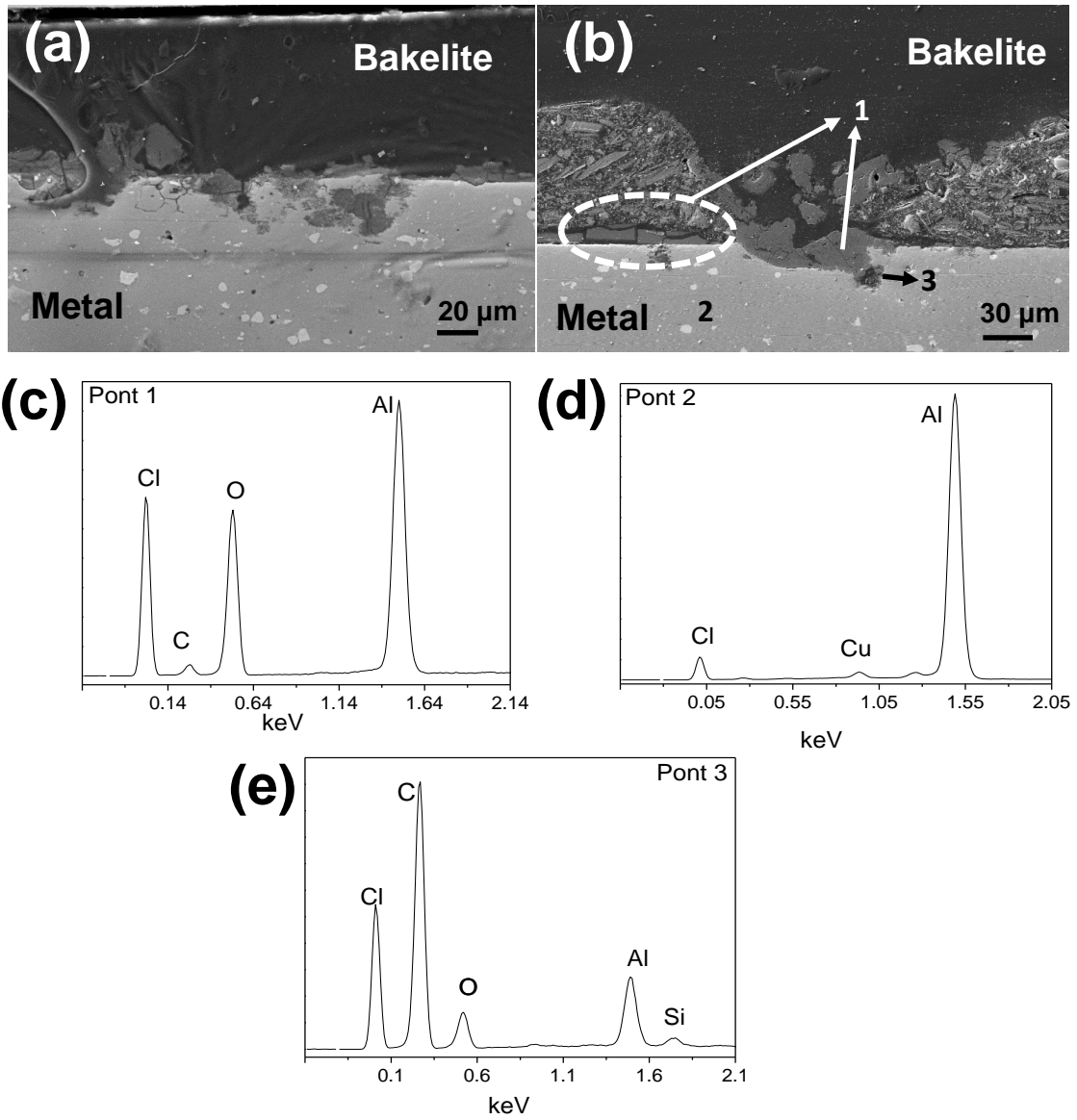
Figure 8

Figure 9

Figure 10