



Corrosion protection of galvanized steel by polyimide coatings: EIS and SEM investigations

E. Huttunen-Saarivirta^{a,*}, V.E. Yudin^b, L.A. Myagkova^b, V.M. Svetlichnyi^b

^a Department of Materials Science, Tampere University of Technology, P.O. Box 589, FI-33101 Tampere, Finland

^b Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoy Prospekt 31, 199004 St. Petersburg, Russia

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ABSTRACT

Coatings of two types of polyimides (PI), as poly(4,4'-oxydiphtalic anhydride-co-2,5-bis(4,4'-methylenedianiline)-1,4-benzoquinone) (AQ) and poly(pyromellitic dianhydride-co-4,4'-oxydianiline) (PM), were synthesized on galvanized steel panels and studied and compared in terms of chemical structure, microstructure and corrosion performance in 0.5M NaCl solution. Infra-red spectroscopy, scanning electron microscopy and in situ electrochemical impedance spectroscopy were employed in the investigations. The results showed that, although both studied PI coatings provided the galvanized steel substrate with corrosion protection during the test period, there were evident differences in electrochemical behaviour of the coatings, which could be primarily explained by the different nanostructures. FE-SEM examinations revealed AQ PI coating to be heterogeneous and discontinuous but PM PI coating homogeneous and continuous in nanostructure. Electrochemical behaviour of AQ PI coated galvanized steel obeyed that of a defect-containing coating and indicated gradual decrease in protectivity. In contrast, PM PI coating behaved like a defect-free coating and it provided the galvanized steel substrate with effective corrosion protection all through the 960 h test. The explanations for these observations and the mechanisms of coating damage are discussed in this paper.

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1. Introduction

Protecting reactive metals by covering their surface with organic coatings is an attractive means of combining the mechanical properties of metals and alloys and the surface characteristics of the coatings. The desired surface properties of the organic coatings may be corrosion resistance, wear resistance, colour, electronic insulation and/or noise reduction, and these are applied particularly on steel, aluminium and galvanized steel [1]. Polyimides are considered high-performance polymer materials, due to their excellent thermal stability, good mechanical properties, outstanding electrical properties and chemical stability [2–4], i.e., they provide many of the (surface) characteristics that are pursued by the use of organic coatings. However, polyimides are quite sensitive to water, due to possible hydrolysis of imide rings. Recent studies of Han et al. [5–7] have shown that coatings of amine-quinone polyimides, i.e., polyimides containing the 1,4-benzoquinone functional group, can protect iron against corrosion in a NaCl containing electrolyte much better than conventional polyimide coatings. The inhibiting effect of poly(amine-quinone)s has been attributed to the abundance of p-electrons and unshared electrons on the nitrogen atom, which

can interact with the d-orbitals of iron to form a coordinate bond [5,8].

Despite the intensive work that has been carried out in the field of developing new corrosion-resistant polyimide coatings on metals, two evident gaps in the knowledge exist: first, little emphasis has been put on understanding the role of synthesized coating microstructure in the corrosion protection properties and, second, the coatings have been deposited only on iron, i.e., no studies so far have reported on amine-quinone polyimide coatings on galvanized steel or aluminum substrates. This paper addresses to these two important research issues. Hence, in this study, the corrosion protection properties of two types of polyimides: a new amine-quinone polyimide, as poly(4,4'-oxydiphtalic anhydride-co-2,5-bis(4,4'-methylenedianiline)-1,4-benzoquinone), and a conventional polyimide, as poly(pyromellitic dianhydride-co-4,4'-oxydianiline) on galvanized steel substrate were investigated and compared in terms of structure and electrochemical behaviour.

2. Experimental procedures

2.1. Materials

In this study, two types of polyimides, a new amine-quinone polyimide, as poly(4,4'-oxydiphtalic anhydride-co-2,5-bis(4,4'-methylenedianiline)-1,4-benzoquinone), Fig. 1a, and a

* Corresponding author. Tel.: +358 40 849 0134; fax: +358 3 3115 2330.
E-mail address: elina.huttunen-saarivirta@tut.fi (E. Huttunen-Saarivirta).

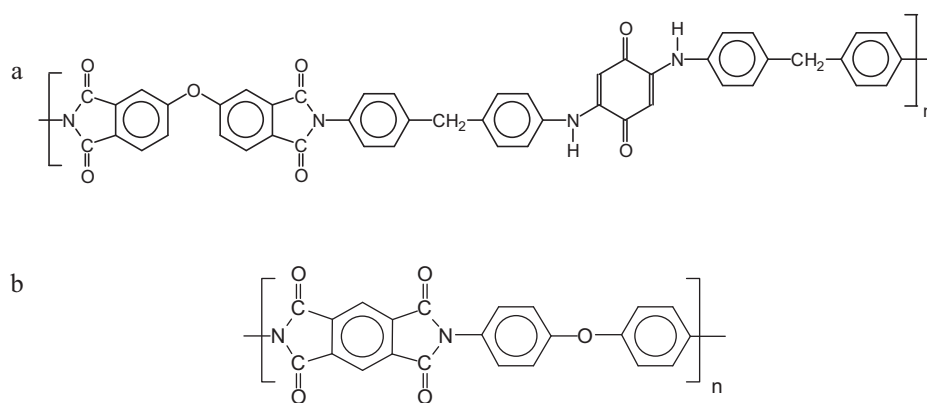


Fig. 1. Molecular structure of the synthesized polyimide coatings. (a) AQ PI coating. (b) PM PI coating.

conventional polyimide, as poly(pyromellitic dianhydride-co-4,4'-oxydianiline), Fig. 1b, were synthesized.

In the synthesis of amine-quinone polyimide, monomers of 2,5-bis(4,4'-methylene dianiline)-1,4-benzoquinone (AQMDA) were first prepared from 4,4'-methylene dianiline and 1,4-benzoquinone via Michael addition, as described in [6]. The structure of the new monomer (AQMDA) was confirmed by means of ^1H NMR, ^{13}C NMR and IR spectroscopy. Amine-quinone polyimide (AQ PI) was then prepared by the polycondensation process of AQMDA and 4,4'-oxydiphtalic anhydride (ODPA) in *N*-methyl-2-pyrrolidinone (NMP), as shown in Fig. 2. ODPA was purchased from Aldrich and recrystallized before synthesis of the polyimide.

A conventional polyimide was made from 4,4'-oxydianiline and pyromellitic dianhydride by the same synthetic procedure as for AQ PI. Both used reagents were purchased from Aldrich and were recrystallized before synthesis of PI.

In the synthesis of both types of polyimide coatings, viscous solutions of the poly(amic acid)s of PM and AQPI at 15 wt.% solid

Table 1

Comparison of the thermal and mechanical properties of the two types of synthesized polyimides.

	AQ PI	PM PI
T_d ($^{\circ}\text{C}$) ^a	550	575
T_g ($^{\circ}\text{C}$) ^b	305	378
Tensile strength (MPa) at RT	96 ± 4	135 ± 2
Young modulus (GPa) at RT	3.0 ± 0.1	3.1 ± 0.2
Elongation at break (%) at RT	5.3 ± 0.6	56 ± 7

^a Temperature at which 10% weight loss occurred in argon.

^b Glass transition temperature, estimated as temperature of maximum of loss modulus at DMA curve.

concentration in NMP were spread onto 50 mm $\times$ 50 mm $\times$ 2 mm galvanized steel panels with the aid of a spin coater. The galvanized steel was of the type of GR43A/ASTM-A36, and the surface of the panels was cleaned using NMP and dried before application of the coatings. After the coating solutions were spread on the panels,

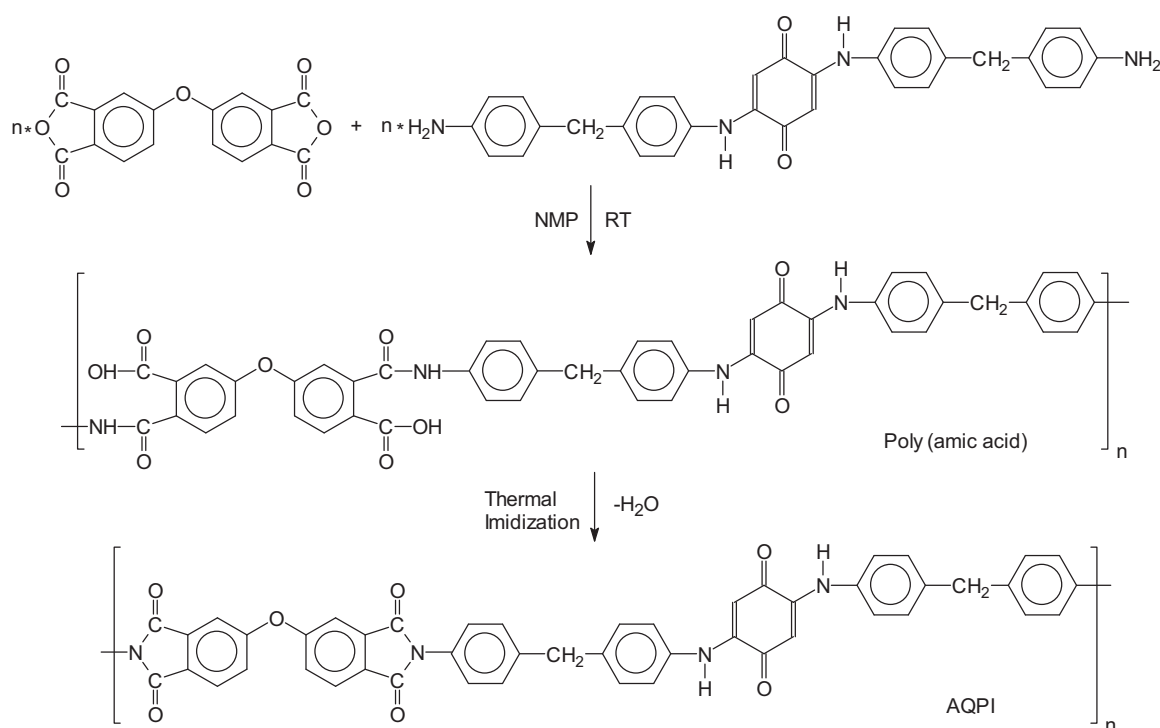


Fig. 2. Two-stage synthesis of the amine-quinone polyimides.

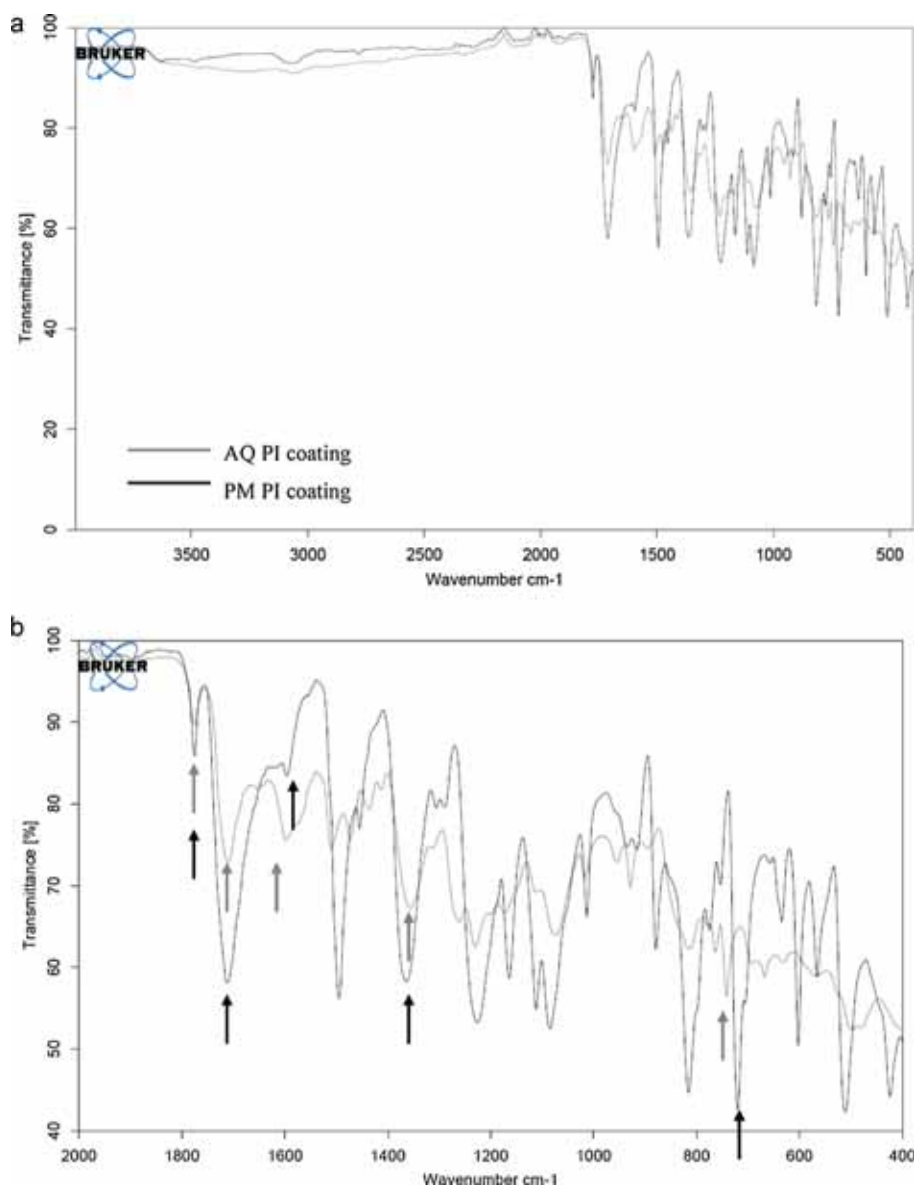


Fig. 3. IR spectra (a) overview and (b) focusing on the 500–2000 cm^{-1} range for AQ PI and PM PI coated galvanized steel panels. Arrows indicate the important and specific peaks.

the specimens were dried at 80 °C for 24 h, after which the formed coatings were thermally imidized under nitrogen atmosphere by successive heating at 50 °C for 1 h, then at 150 °C for 1 h, at 250 °C for 1 h and finally at 290 °C for 1 h. Additional heating at 350 °C for 15 min were made for PM coatings to finalize the process of imidization. The thickness of both types of PI films on the galvanized steel panels was $10 \pm 1 \mu\text{m}$.

For determination of thermal and mechanical properties of the PI coatings, small amounts of the poly(amic acid)s of AQ and PM PI were cast onto glass plates and dried and imidized as reported above. The coatings on glass were soaked in water, to obtain free-standing films of $\sim 40 \mu\text{m}$ thickness. Table 1 presents a summary of the key properties of the two types of PI films. The reported values show that the thermal parameters, as temperature of decomposition (T_d) and glass transition temperature (T_g), were slightly higher for PI PM films. As for the mechanical properties, the films had almost equal Young moduli, but PM PI films were evidently more flexible than AQ PI films, indicated by about one order of magnitude higher elongation at break. This may also explain the higher tensile strength of PM PI films as compared to that of AQ PI films.

2.2. Methods

The synthesized coatings on galvanized steel were characterized in terms of their structure and electrochemical behaviour. Chemical structure of the coatings was studied by infra-red (IR) spectroscopy, to provide information on functional groups that were present in the synthesized coatings, and microstructure was studied by scanning electron microscopy (SEM), to introduce knowledge on the integrity and surface morphology of the coatings. IR studies were carried out using a Bruker Optics Tensor 27, through wave number area from 4000 to 400 cm^{-1} . Microstructural examinations were performed using a field-emission (FE) SEM Zeiss ULTRApplus at an acceleration voltage of 5 kV.

Electrochemical impedance spectroscopy (EIS) was used to investigate the corrosion protection afforded by the two polyimide coatings for galvanized steel substrates. EIS experiments were carried out in situ in 0.5 M NaCl solution, the pH value of which was 6.3, using a classical three-electrode cell with a working electrode with an exposed area of about 1 cm^2 , a silver-silver chloride (Ag/AgCl) reference electrode and a platinum counter electrode as well as a

Gamry Instruments potentiostat G750. Gamry Instruments EIS300 Software measured the impedance in the frequency range of 5 mHz to 100 kHz by applying an AC voltage with an amplitude of 10 mV around the corrosion potential. The measurements were performed as a function of immersion time, up to 960 h of immersion. Before the first measurement, the system was let to stabilize for 30 min. Gamry Echem Analyst program was used to analyze the impedance data and to fit the equivalent circuit models. After the test, the specimens were examined using a Philips XL-30 SEM equipped with EDAX energy-dispersive spectrometer (EDS), to yield data on possible degradation mechanisms of the coatings.

3. Results

3.1. Structure of the coatings

IR spectra for the AQ and PM PI coated galvanized steel panels are shown in Fig. 3. It can be seen that the C=C and C=O peaks, which are generally located at 1622 and 1732 cm^{-1} , respectively, were detected at 1598 and 1711 cm^{-1} in the case of AQ PI coated galvanized steel. These peaks confirm that the coating contains the diamino-1,4-benzoquinone group. The spectrum also had characteristic imide bands near 1778 cm^{-1} (coupled carbonyls), 1371 cm^{-1} (CN stretching) and 765 cm^{-1} (cyclic structures) as indicated in Fig. 3. In the case of PM PI coated galvanized steel, the spectrum of coating contained characteristic imide absorption bands at 1775 and 1712 cm^{-1} (C=O), 1364 cm^{-1} (C–N) and 720 cm^{-1} (imide ring). IR spectra measured on the films confirm the complete conversion of coatings from poly(amic acid)s to polyimides.

FE-SEM studies on PI coated galvanized steel disclosed that the surface of AQ PI coating was relatively heterogeneous in nanostructure, whereas that of PM PI coatings was very homogeneous (Fig. 4). The heterogeneous structure of AQ PI coating, Fig. 4a, may be due to a relatively high solid contents, 15 wt.%, of the poly(amic acid)s in NMP, as compared to that employed in other studies, 5–10 wt.% [5,6]. Furthermore, FE-SEM studies revealed occasional pores or discontinuities in AQ PI (Fig. 4b) coatings but no pores or discontinuities in PM PI coatings (Fig. 4c). It is emphasized that although the coating thicknesses were the same, FE-SEM studies clearly demonstrated that the thickness variation was greater in the case of AQ PI coating, evidently due to rougher surface morphology.

3.2. Corrosion protection by the coatings

AQ and PM PI coated galvanized steel panels were exposed to 0.5 M NaCl electrolyte for 960 h and the electrochemical behaviour was monitored in situ by electrochemical impedance spectroscopy (EIS), by applying small-amplitude alternating potential signal of varying frequency on the specimens and by collecting and analyzing the response on current values. Figs. 5 and 6 show EIS spectra for AQ and PM PI coated galvanized steel, respectively, as a function of immersion time, together with the initial spectra for uncoated substrate. Bode magnitude plot for uncoated substrate (Figs. 5a and 6a) disclosed very low overall impedance values, with the low-frequency-end value being $4.6 \times 10^2 \Omega \text{ cm}^2$. Application of AQ PI coating resulted in very high initial impedance values, with a low-frequency-end value of $8.3 \times 10^{10} \Omega \text{ cm}^2$, probably following a barrier effect. However, impedance values for AQ PI coated surface decreased significantly with increase in immersion time, particularly at low frequencies, referring to decrease in pore resistance values of the coating. Bode phase angle plot for the uncoated substrate (Figs. 5b and 6b) showed two clearly distinguished maxima at about 2510 and 0.15 Hz, referring to two time constants, consistent with results of Arenas and de Damborenea [9]. Of these two

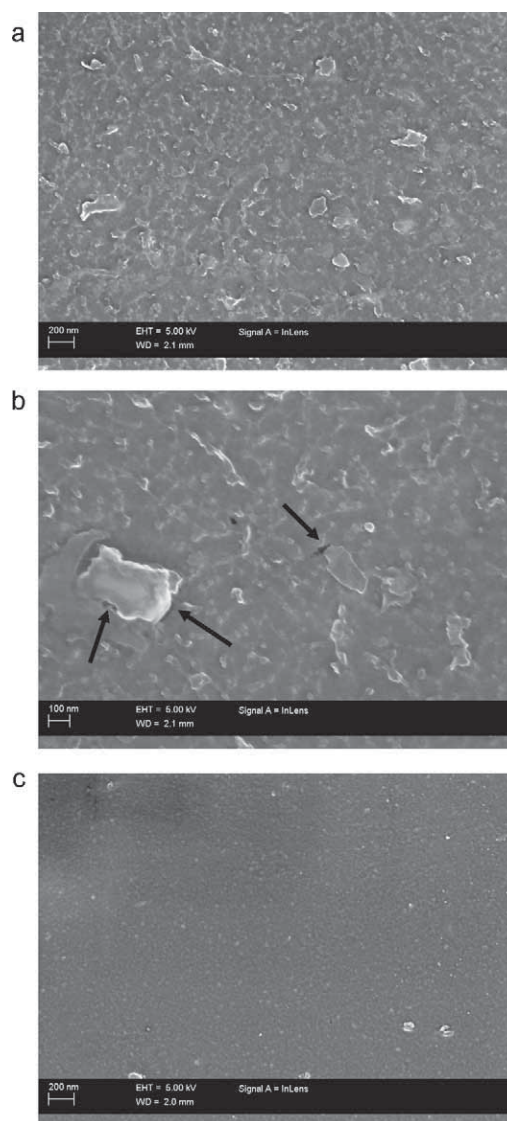


Fig. 4. FE-SEM images, showing surface of the PI coatings. (a) AQ PI. (b) A mode detailed view of AQ PI, with the arrows indicating discontinuities. (c) PM PI.

phase angle maxima, the high-frequency one has been reported to be related to the presence of an oxide layer on the metal surface, while the low-frequency one has been connected to the adsorption of $\text{Zn}^{\text{I}}_{\text{ads}}$, which controls the overall zinc dissolution process [9]. In contrast, AQ PI coating behaved initially almost like a capacitive coating, with a relatively constant phase angle of -90° at all except for the lowest frequencies (Fig. 5b). However, with increase in immersion time, the phase angle plot for AQ PI coated surface became clearly different from that initially observed: the overall angle values decreased, particularly at high frequencies, and only after 168 h of immersion, a clear peak was introduced in the plot at about 0.1 Hz, consistent with uncoated substrate undergoing corrosion. This indicates that some electrolyte might have penetrated the coating and caused under-coating corrosion. Nyquist plot for the AQ PI coated galvanized steel (Fig. 5c) disclosed that the coating did not initially behave in a purely capacitive manner but, instead, was under charge transfer control after all immersion times. As evaluated on the basis of diameters of the semi-circle shaped curves in Z_{real} axes, polarization resistance of the AQ PI coated surface decreased with increase in immersion time, but was, in all cases, higher than for the uncoated substrate, indicative of AQ PI coating providing the substrate with corrosion protection.

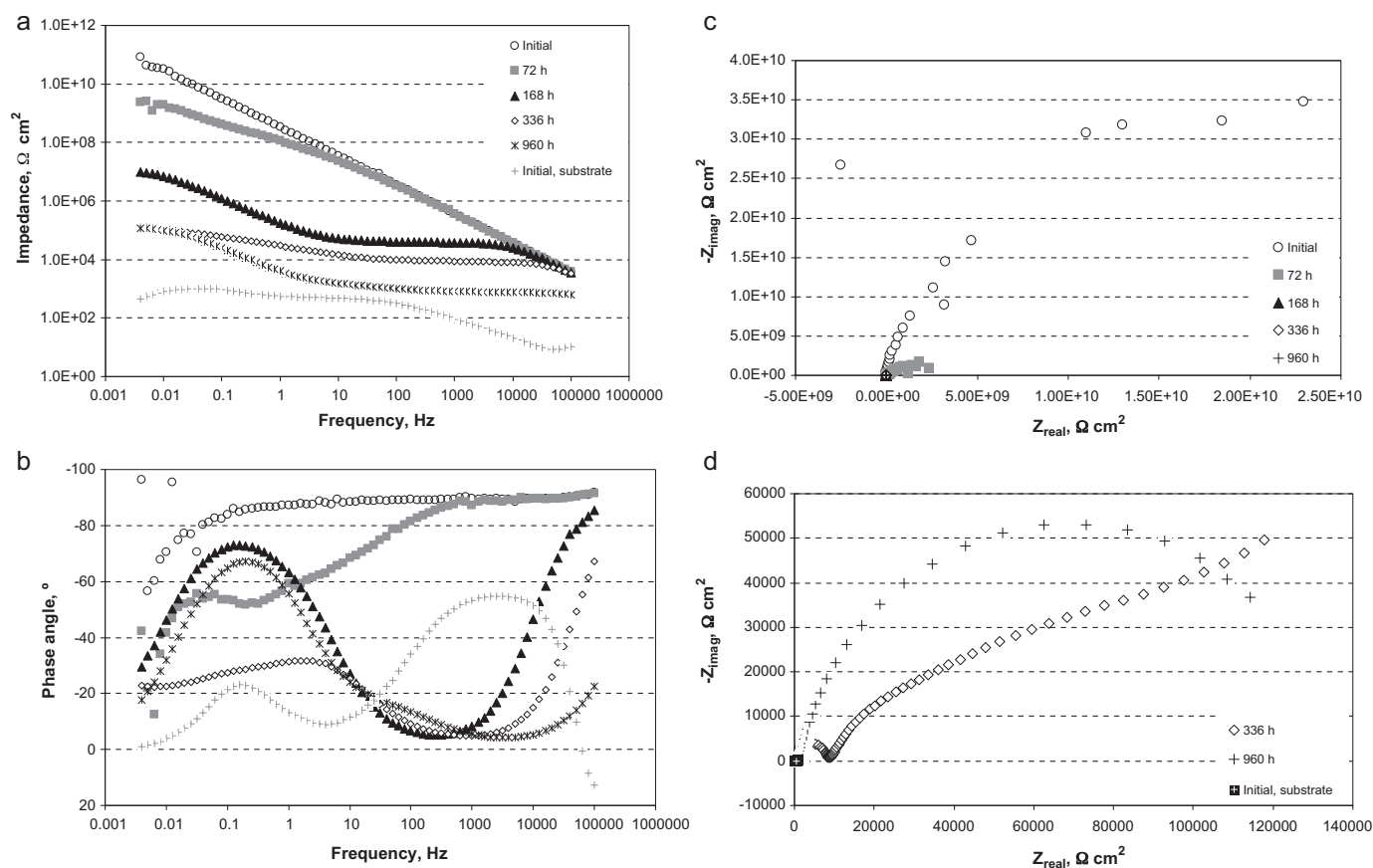


Fig. 5. EIS spectra for AQ PI coated galvanized steel after different immersion times in 0.5 M NaCl and, for comparison, for the bare substrate initially. (a) Bode magnitude plot. (b) Bode phase angle plot. (c and d) Nyquist plot.

Fig. 6 shows very high overall impedance values for PM PI coated galvanized steel at all frequencies, irrespective of exposure time, and a low-frequency-end value of $1.0 \times 10^{11} \Omega \text{ cm}^2$ both initially and after 960 h of exposure to 0.5 M NaCl solution. These results indicate that, first, applying PM PI coating on the substrate significantly increased the measured impedance and, second, the electrochemical behaviour of PM PI coating was virtually independent of immersion time, because the bode magnitude plot recorded at the end of the test period was almost identical to that measured initially. The latter further suggests that only negligible changes had occurred in the coating properties during the immersion period. Bode phase angle curves (Fig. 6b) for PM PI coated galvanized steel disclosed that, initially, the values were retained at about -90° throughout the studied frequency range, suggesting the coating behaves in a capacitive manner, i.e., like a dielectric. However, with increase in immersion time, the phase angle values for PM PI coated galvanized steel shifted from the original value of -90° towards slightly lower values, particularly at high frequencies, indicating that some slight changes in the coating properties might have happened. Nyquist presentation of EIS data (Fig. 6c) revealed that PM PI coated galvanized steel did behave almost in a capacitive manner at all immersion times, because the shape of the curves resembled more a straight line perpendicular to the real axis than a semi-circle.

The surface processes that occur on specimens may be simulated by resistive-capacitive electrical networks, by fitting appropriate equivalent circuits to impedance plots using an analysis software and by quantification of the characteristic values for the network components. Fig. 7 shows the two electrical equivalent circuits that model the electrochemical behaviour of AQ and PM PI coated gal-

vanized steel exposed to 0.5 M NaCl solution. The simpler of the two equivalent circuits, Fig. 7a, is for a defect-free organic coating and fits well the EIS data of PM PI coated galvanized steel after all immersion times. A model circuit for a defect-containing organic coating, Fig. 7b, simulates the electrochemical behaviour of AQ PI coated galvanized steel. Both presented models employ constant phase elements (CPE) instead of capacitors, with CPE equaling to $1/C(j\omega)^\alpha$, where α is the frequency dispersion factor and varies from 1 to 0 (when $\alpha = 1$, C can be considered a real capacitance), j is the square root of -1 and ω is the angular frequency.

The evolution of electrical network parameters: pore resistance R_{po} , CPE parameter α and coating capacitance C , calculated from obtained CPE value, that have been determined by numerical fitting of the models to the experimental spectra for the AQ and PM PI coated galvanized steel is shown in Fig. 8. In general, AQ PI coated surface was characterized by much lower pore resistance values than PM PI coated surface, Fig. 8a. Furthermore, pore resistance value for AQ PI coated galvanized steel decreased dramatically, by more than 7 orders of magnitude, during the first third of the test, being followed by relatively constant resistance values of about $2-3 \times 10^3 \Omega$ until the end of the test. In the case of PM PI coated galvanized steel, pore resistance values were relatively constant, at about $2-3 \times 10^{14} \Omega$, all through the test. These results clearly indicate that PM PI coating protects the galvanized steel substrate better than does AQ PI coating. Comparison of CPE parameter α reveals a slight decrease during the test in the case of both PI coatings but somewhat lower overall values for AQ PI (0.99–0.90) than for PM PI coating (0.99–0.96), consistent with PM PI coating behaving almost in a capacitive manner, as described above. The coating capacitance values for AQ PI coating were, at the beginning of the

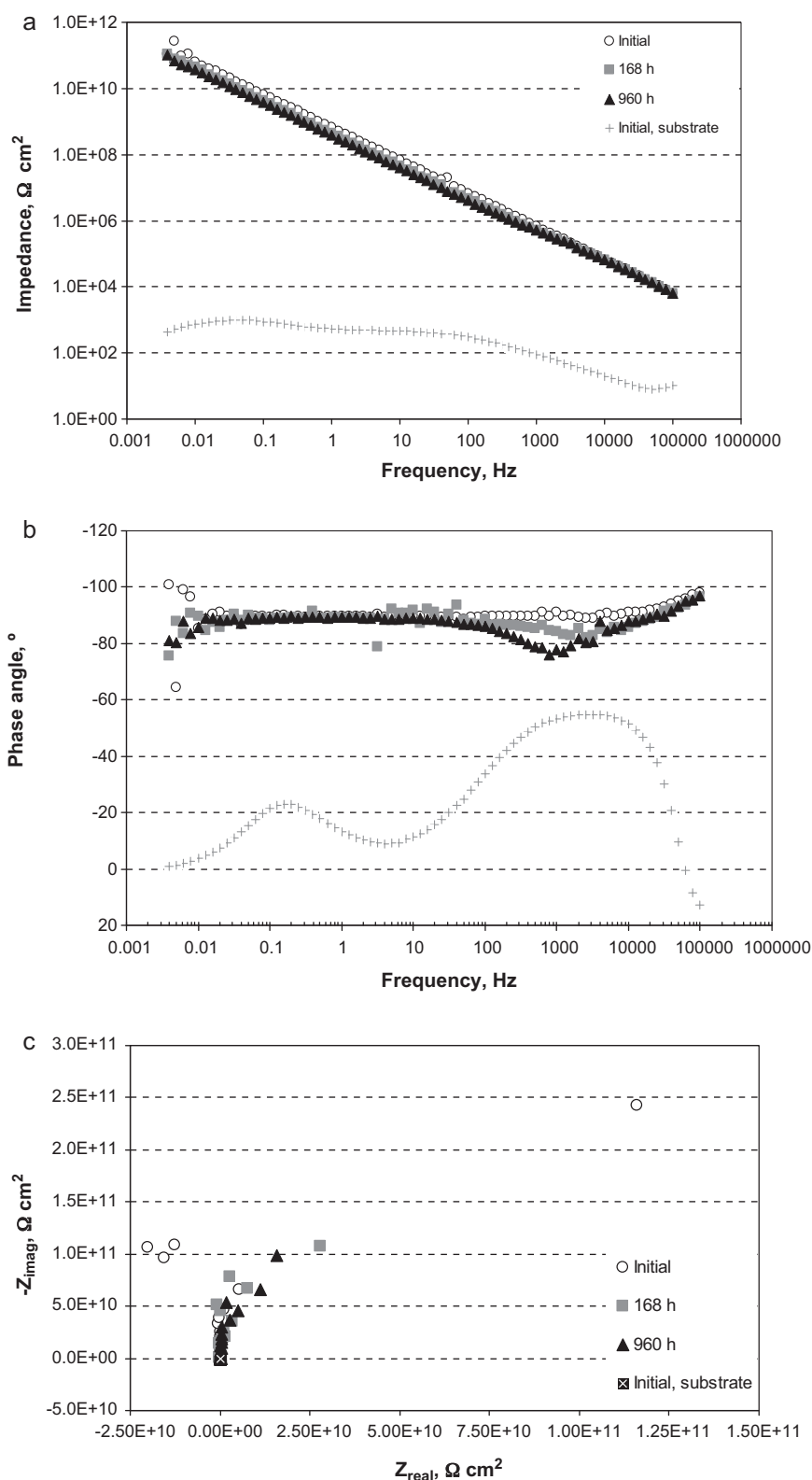


Fig. 6. EIS spectra for PM PI coated galvanic steel after different immersion times in 0.5 M NaCl and, for comparison, for the bare substrate initially. (a) Bode magnitude plot. (b) Bode phase angle plot. (c) Nyquist plot.

test, slightly higher than those for PM PI coating, but showed a significant decrease during the second third of the test, giving much lower capacitance values for AQ PI coating than for PM PI coating during the last third of the test. The overall decrease in capacitance value for AQ PI coating may be due to delamination of the coat-

ing, and, probably, due to the following presence of an electrolyte layer on the surface, as earlier reported e.g., by Deflorian et al. [10]. In contrast, in the case of PM PI coating, coating capacitance values slightly increased with test propagation, which is essentially a more typical trend for coatings.

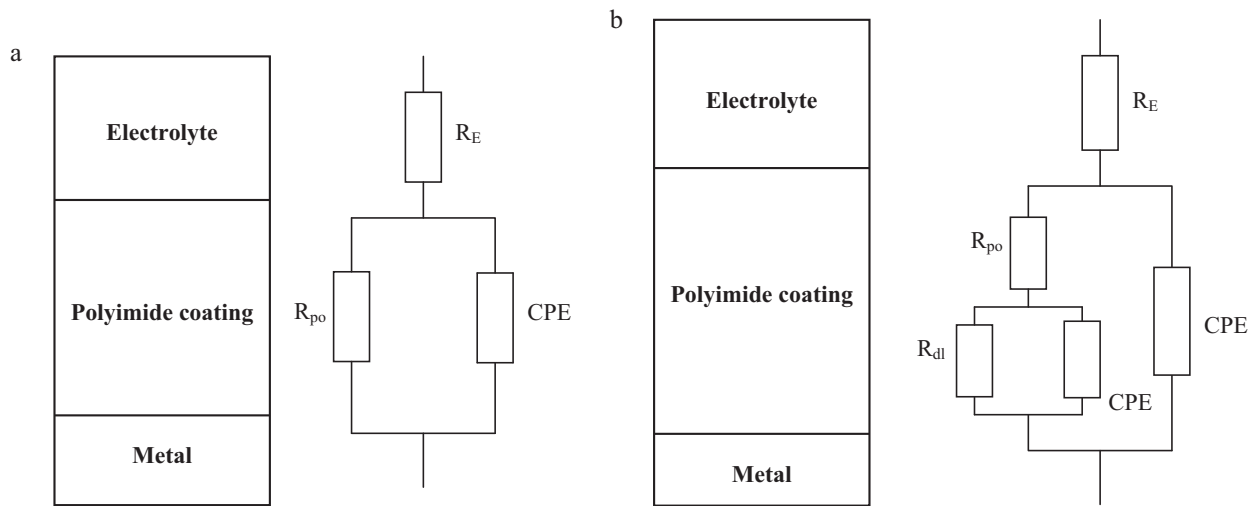


Fig. 7. Equivalent electrical circuits for polymer-coated metals. (a) A defect-free coating. (b) A defect-containing coating. R_E is resistance by electrolyte, R_{po} is coating pore resistance, CPE is constant phase element, R_{dl} is double layer resistance.

It has been reported [11,12] that during the first 24–72 h of immersion, filling of the coating pores and defects with the electrolyte causes a decrease in pore resistance values. In this study, the initial decrease in pore resistance values for AQ PI coating occurred within a much longer time period than what is reported for fill-

ing the coating pores and defects with electrolyte, indicating that the observed decrease was not only due to electrolyte transport into coating discontinuities but also because of coating degradation. In contrast, in the case of PM PI coating, a slight decrease in pore resistance values could be detected during the first 24–72 h

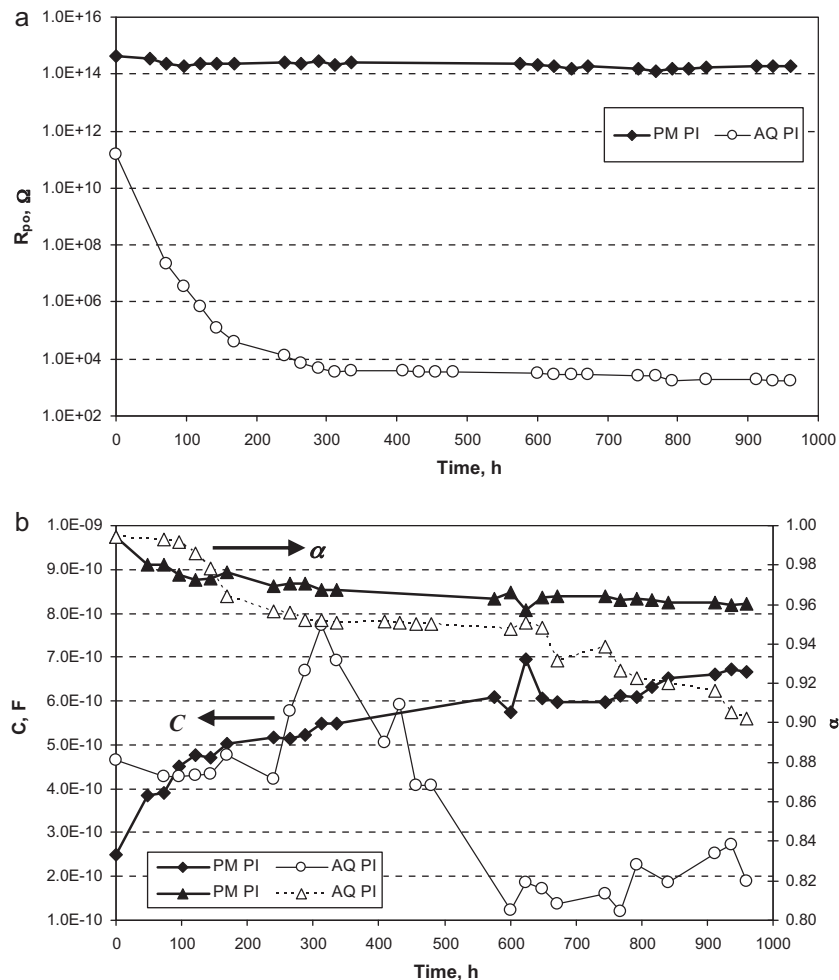


Fig. 8. The evolution of electrical network parameters for the AQ and PM PI coated galvanized steel panels. (a) Pore resistance. (b) Coating capacitance and CPE parameter α .

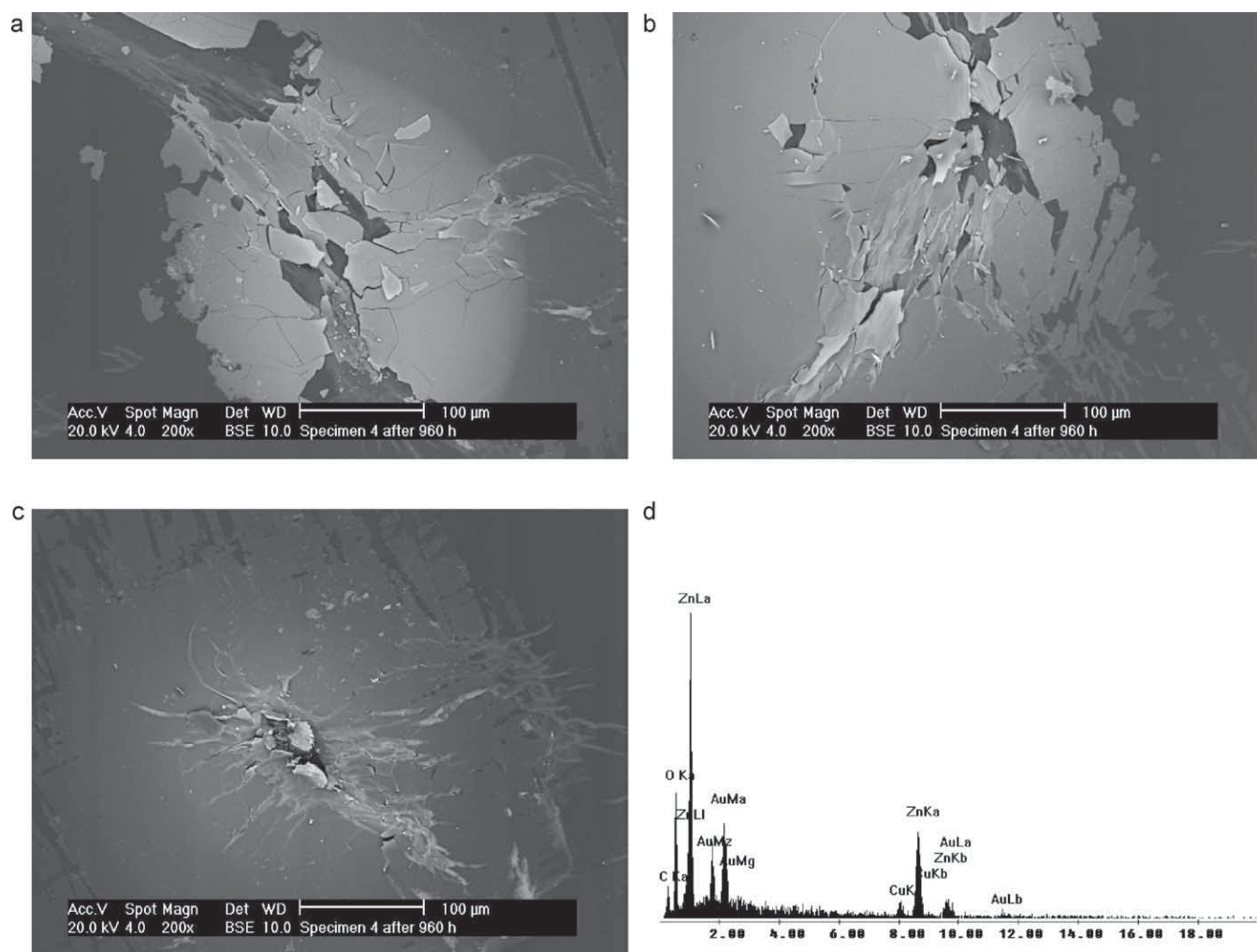


Fig. 9. SEM images (a–c) and EDS spectrum (d) of AQ PI coated galvanized steel after 960 h of immersion in 0.5 M NaCl. The presence of Au in EDS spectrum is reasoned by the fact that before the exposed specimen was brought to SEM, it was coated by a thin conductive gold layer by sputtering, to ensure electrical conductivity.

of the test; this might, indeed, originate from electrolyte penetration in the coating discontinuities. This is consistent with the observation of apparent changes in the coating capacitance values for AQ PI coated surface, suggesting instability, i.e., dissolution or delamination of the coating [13] and relatively steadily developing capacitance values for PM PI coating, indicating stable coating behaviour.

After immersion of 960 h in a 0.5 M NaCl solution, the PI coated specimens were examined visually and by SEM. Visual examination revealed some local delamination of AQ PI coating within the exposed area but no damage in PM PI coating. Further studies by SEM disclosed zinc oxide between AQ PI coating and the galvanized steel substrate, apparently resulting in the delamination of the coating at and around such areas (Fig. 9). Indeed, coating delamination has been reported to be a predominant corrosion mechanism for the organic coating-galvanized steel system following degradation of the coating [1]. This observation is also consistent with a peak in a Bode phase angle plot at a frequency characteristic for zinc corrosion process, i.e., under-coating corrosion. In turn, SEM investigations on PM PI coated galvanized steel (Fig. 10) showed the presence of some NaCl on top of the PM PI coating, suggesting that some electrolyte had dried and retained on the PM PI coating after the test. However, neither the EIS spectra nor the SEM examinations revealed any NaCl between the coating and the substrate, i.e., no degradation of the coating or under-coating corrosion were detected.

4. Discussion

The presented results show that application of both types of coatings, AQ and PM PI, significantly improves the corrosion performance of galvanized steel in 0.5 M NaCl solution, particularly at the early stages of exposure. Concerning the relative superiority of the organic coatings, it is expected that AQ PI coating protects the underlying galvanized steel more effectively than PM PI coating, due to improved adhesion following interaction between the 2,5-diamino-1,4benzoquinone group and the substrate [5,8]. In this study, the opposite is observed, i.e., PM PI coating effectively protects the galvanized steel against corrosion in 0.5 M NaCl solution for the whole test period, 960 h, while AQ PI coating of an equal thickness degrades during the exposure period, enabling under-coating corrosion and coating delamination. Such discrepancy between the expected and observed behaviour of the coatings may be explained by their different nanostructures: AQ PI coating of this study is relatively heterogeneous and slightly discontinuous, while PM PI coating is very homogeneous and continuous. These coating characteristics probably originate from synthesis conditions of the coatings, particularly from the used solid contents of poly(amic acid)s in NMP, that was 15 wt.% in the case of both types of PIs included in this study. Earlier [5,6], excellent corrosion protection by AQ PI coatings has been reported after the synthesis of coatings using 5–10 wt.% solids in the synthesis of poly(amic acid)s in NMP.

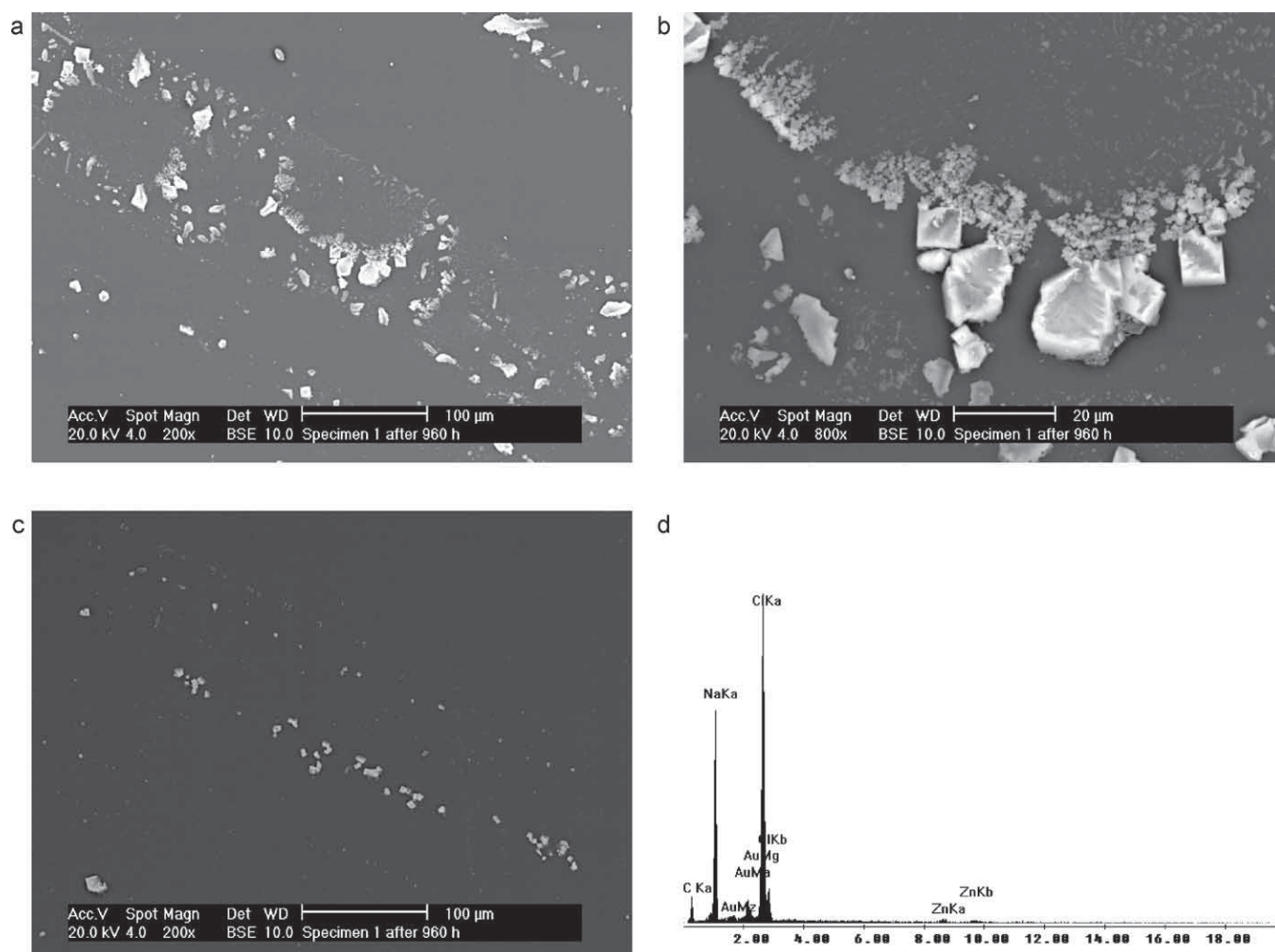


Fig. 10. SEM images (a–c) and EDS spectrum (d) of PM PI coated galvanized steel after 960 h of immersion in 0.5 M NaCl. The presence of Au in EDS spectrum is reasoned by the fact that before the exposed specimen was brought to SEM, it was coated by a thin conductive gold layer by sputtering, to ensure electrical conductivity.

In general, the mitigation of corrosion by organic coatings is due to a barrier effect for ions, adhesion of the coating, blocking of ionic baths between local anodes and cathodes along the metal/polymer interface and a network of corrosion active pigments and inhibitors. In turn, corrosion of a polymer-coated metal requires the penetration of water molecules, ions and oxygen to the interface. The diffusion of these species follows small pores or defects within the organic coating and leads to the contact between the corrosive electrolyte and the substrate and, eventually, to corrosion along the coating-metal interface [1]. The results presented in this study show that some detectable defects appear in AQ PI coating, evidently enabling travel of electrolyte through the coating to the substrate surface. Besides evident changes in EIS spectra for AQ PI coated surface and following decrease in pore resistance values obtained by modelling, electrolyte penetration was evidenced by SEM observations on under-coating corrosion. In the case of PM PI coating, no pores or defects were revealed in FE-SEM examinations and the coating acted well as a barrier against electrolyte penetration.

It is emphasized that the results obtained from FE-SEM characterization also explain the relatively poorer thermal and mechanical properties of AQ PI films as compared to those of PM PI films (Table 1). Han and Nikles [6] have demonstrated that both thermal and mechanical properties of AQ PI films may be modified by the synthesis conditions, which is probably due

to influence of the synthesis conditions on film microstructure. Indeed, in future, more attention should be paid on understanding the connection between coating synthesis conditions, coating structure and coating performance, despite the fact that the first step alone, particularly synthesis of new organic compounds, faces several challenges. Advanced characterization techniques, such as FE-SEM and EIS, are in a key role in such studies.

5. Conclusions

In this study, two organic coating systems: a new amine-quinone (AQ) polyimide (PI) and a conventional (PM) PI coated galvanized steel, are studied and compared in terms of structure and corrosion performance in 0.5 M NaCl solution. Infra-red spectroscopy and scanning electron microscopy were used to characterize the chemical structure and microstructure of the coatings, respectively, while in situ electrochemical impedance spectroscopy was used to investigate the electrochemical behaviour of the coated panels for 960 h. The presented results allow the following conclusions to be drawn:

Although synthesized via similar process routes to equal thickness, AQ PI and PM PI coatings are different in nanostructure. AQ PI coating is heterogeneous and slightly discontinuous, while PM PI coating is very homogeneous and continuous.

Both coatings provide galvanized steel substrate with corrosion protection during the test period, evidently by a barrier effect.

Discontinuities, i.e., pores and defects, in AQ PI coating enable electrolyte penetration to the coating-substrate interface, as indicated by a radical decrease in pore resistance values during the first third of the test, introducing under-coating corrosion and following coating delamination. Electrochemical behaviour of AQ PI coated galvanized steel obeys that of a defect-containing coating.

PM PI coating provides galvanized steel substrate with effective corrosion protection all through the 960 h test, as suggested by very high and stable pore resistance values. The coating system behaves like a defect-free coating, with no indications of coating failure in EIS or SEM studies being revealed.

In future, more emphasis has to be put on understanding the interplay between the synthesis conditions for new organic coatings and the resulting coating structure and performance. Advanced and sensitive characterization techniques, such as FE-SEM and EIS, play a key role in such studies.

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