

Final Draft
of the original manuscript:

Scharnagl, N.; Blawert, C.; Dietzel, W.:

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In: Surface & Coatings Technology (2008) Elsevier

DOI: 10.1016/j.surfcoat.2008.11.018

Corrosion Protection of Magnesium Alloy AZ31 by Coating with Poly(ether imides) (PEI)

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Abstract

To improve the corrosion performance of the magnesium alloy AZ31 the possibilities of obtaining suitable surface protection by polymer coatings was studied. In the present investigation, the commercially available class of poly(ether imides) was used to this end. The coatings were applied to the metal surface by dipping yielding both porous and non-porous layers. The resulting coatings were tested under environmental conditions in salt-spray and climate exposure tests. The corrosion resistance and the degradation behaviour were investigated using electrochemical impedance spectroscopy (EIS). Furthermore, the resulting polymer coatings were qualified by ATR-IR and IR microscopy.

Keywords: Poly(ether imide); PEI; Corrosion; Magnesium; AZ31; Polymer coating; EIS

Introduction

Advantageous properties make magnesium a promising choice for a number of applications. It has a high strength/weight ratio with a density 30% less than aluminium and 25% of that of iron. Additionally, it has good machinability, high thermal conductivity, high dimensional stability and can be easily recycled [1]. Therefore, it is valuable in a wide range of applications in automotive, aerospace, computer, handheld or household industry. Magnesium has further been suggested for use as an implant metal due to its low weight and inherent biocompatibility [2, 3].

However, besides the promising aspects one can not ignore the number of undesirable properties which make magnesium and its alloys less usable for a number of applications. Poor corrosion resistance as well as high chemical reactivity are the main factors that hinder its widespread use. Magnesium alloys and magnesium itself are highly susceptible to galvanic corrosion, which may lead to severe corrosion in the metal and therefore decrease its mechanical stability. This behaviour can not only be reduced by alloying, e.g. adding rare-earth elements to the alloys [4] and/or by use of high purity alloys which are the only suitable

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techniques to control general corrosion. In general, the elimination of flux inclusions, surface contamination and galvanic couples are other ways to reduce the corrosion tendency. The elimination of impurities can be obtained effectively by surface cleaning and pre-treatment [5]. Subsequent coating can prevent galvanic corrosion in contact with other metals.

Various coating and surface treatment techniques are available for magnesium, such as plating, anodizing, conversion coating, and polymer coating to name the most important ones. Each has its own advantages and disadvantages. The various methods were reviewed in detail by Gray et al[6]. Among these, polymer coating seems to be a promising technique. Depending on the type of polymer it combines corrosion protection, enhancement of abrasion and wear properties. During the last years polymer systems have been commonly used for other metals like aluminium or steel. This includes polymers based on acrylic systems, polypyrroles, polyanilines and several types of polyesters.[5, 7-16] However, for magnesium and magnesium alloys these were mostly not successful. A number of reasons can be identified, among these a low stability in alkaline environment existing at aqueous $Mg(OH)_2$ surfaces, low UV resistance, brittleness and low adhesion properties on the magnesium surface. Another drawback of the above polymer classes is their bioincompatibility which makes them inoperative to medical applications.

In the case of poly(ether imide) (PEI) the mechanical properties are in a satisfying compatibility with those of magnesium and its alloys. Additionally, it combines acceptable resistance against environmental influences with the possibility to be prepared as a porous or non-porous coating depending on the solvent system chosen. Together with its further advantage to be chemically modifiable for medical applications, this enables the use for drug delivery systems with controlled release functionality where drug storage and degradation kinetics are important. Albrecht et al.[17] show the reaction of PEI with poly(vinylpyrrolidone) (PVP) for good hemocompatibility. This and the chemical, physical and mechanical properties make the class of poly(ether imides) well suited for protective coatings on magnesium which includes corrosion prevention as well as biocompatibility.

Experimental

Poly(ether imide) Ultem 1000[®] was used as a commercial product obtained from General Electric. Figure 1 gives the chemical structure of the polymer. To perform the coatings, polymer solutions were prepared either in dichloromethane (CH_2Cl_2) or N,N'-dimethylacetamide (DMAc), both of analytical grade. The concentrations were 1 or 3 wt.-% in

the case of CH_2Cl_2 and 10 or 20 wt.-% for DMAc to control the coating thickness by the viscosity of the solution.

The organic corrosion inhibitors salicylaldehyde, 8-hydroxyquinoline, quinaldic acid, and benzotriazole were used as delivered by Sigma-Aldrich. In relation to the PEI content 10% of reactant were added to the coating solution.

Magnesium AZ31 alloy (>96% Mg, <3% Al, <1% Zn) was used as substrate. Prior to coating the metal was pre-treated by different cleaning steps. These include grinding with SiC paper or chemical treatment with a combination of acetic acid/ $\text{Ca}(\text{NO}_3)_2$. After this treatment the samples were washed with deionised water at room temperature and dried in a vacuum oven at 40°C for 2 hours.

Coating was performed by dipping the metal sheets into the polymer solution at ambient temperature. The number of coating steps influences the resulting thickness which was between 1 and 10 μm , also depending on the viscosity of the solution. In the case of dichloromethane being used as solvent, the samples were dried in a vacuum oven at 40°C (10 mbar) for 4 hours. For DMAc the samples were first exposed to environmental conditions to let a phase inversion process of the polymer take place. After this, the samples were also dried at 40°C (10 mbar) for 4 hours in a vacuum oven.

Electrochemical studies were carried out using a computer controlled potentiostat/frequency response analyser (Gill AC, ACM Instruments, UK) to evaluate the performance of the polymer coatings on AZ31 magnesium alloy. A typical three electrode system consisting of a platinum mesh as counter electrode, a Ag/AgCl reference electrode and the specimen (0.5 or 1.54 cm^2 exposed area) as working electrode, was used. The experiments were conducted in aqueous 3.5 wt.-% NaCl solution. Prior to the experiments the samples were exposed for 30 min to the electrolyte to establish a relatively stable open circuit potential. Electrochemical impedance spectroscopy (EIS) experiments were performed at open circuit potential with an AC amplitude of +/-10mV over the frequency range of 30 kHz to 10^{-2} Hz. The EIS tests were repeated after fixed exposure periods between 0,5 h and 96 h.

Salt spray tests were performed with 5 wt.-% NaCl solution for 48 hours according to DIN 50021. Climate tests were performed following the Volvo test specification VCS 1027, 149.

For the IR investigations a Bruker FTIR spectrometer TENSOR and an IR microscope HYPERION 2000 were used. Both are equipped with ATR and reflecting facility.

Results and Discussion

Porous polymer coatings

EIS measurements of bare materials AZ31 and the pure non-porous poly(ether imide) were recorded. As expected, the curves in figure 2 show low impedance ($<100 \text{ Ohm cm}^2$) values and indication of pitting corrosion attack for AZ31 and high impedance ($> 10^8 \text{ Ohm cm}^2$) for the pure polymer. The polymer can be considered as an isolator not dissolving in the present electrolyte. Therefore, in case of a defect free coating on the metal surface the measurement of the free corrosion potential should not result in a defined value. On the other hand, if defects occur the free corrosion potential of AZ31 should be measured. Logically consistent the EIS curve of a defect free coating should behave like the pure non-porous polymer. As a first step coatings with a solution of PEI dissolved in N,N'-dimethylacetamide (DMAc) were performed. As the preparation of these coatings is based on a phase inversion process, the polymer precipitates in the presence of humidity from air and builds a microporous layer (pore size approx. $<0.5\mu\text{m}$). Figure 3 shows the EIS measurements of three samples prepared in different batches. Good reproducibility was achieved, and the impedance reaches the values of pure PEI which is 6 orders of magnitude higher than that of pure AZ31 and therefore shows a huge increase in corrosion resistance. Exposure to salt spray test (figure 4) shows also a good corrosion resistance. While the pure magnesium alloy (figure 4a) is subject to severe corrosion, the coated sample seems to be totally free from any corrosive attack and highly protected. Even a scratched region shows no traces of corrosion. PEI seems to build a kind of passivating layer on the metal, respectively as an intermediate layer between metal and polymer. Albrecht et al.[18] describe a ring opening reaction under the influence of strong bases which might lead to a hydroxamic acid structure (figure 5). Furthermore, Folkers et al. [19] propose a corrosion inhibiting effect by a coordinating species between the hydroxamic acid and a metal oxide (figure 6). Due to the formation of $\text{Mg}(\text{OH})_2$ at the metal surface such an reaction with the PEI might occur and a protective species might be build. In future investigations, this layer and the corresponding reactions will be further studied.

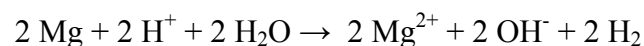
Non-porous polymer coatings

Changing the solvent system for the polymer solution to solvents with lower vapour pressure and higher polarity, like dichloromethane (CH_2Cl_2), will also change the phase inversion. The resulting polymer layer becomes dense, transparent and mostly free of defects. This is a result of the much faster precipitation kinetics which are no longer controlled by an exchange of

solvent and humidity but by evaporation of the solvent. In principle, such a dense and defect-free layer should act as a barrier towards water and electrolyte. Their penetration through micro-defects (in the range of nanometers) would cause swelling of the polymer, a loss in its adhesion and an increase in corrosion activity. If the capillary force in the defects and the osmotic pressure are strong enough a back diffusion of the molecules is hindered and the corrosion products generated from the metal surface, e.g. hydrogen gas, can not be removed at adequate velocity.

Figure 7 shows a time evaluation of a "defect-free" and dense polymer coating on AZ31 by EIS. Already after 1 hour exposure to an aqueous solution of 3.5 wt.-% sodium chloride the curve shows that the impedance level of the pure polymer could not be reached. The level decreases during the next 47 hours from an impedance of about 10^7 Ohm cm^2 to 10^5 Ohm cm^2 . Investigations by IR-spectroscopy and IR-microscopy (figure 8 and 9) confirm the assumption that the polymer layer is not really dense and defect-free. The IR spectrum (figure 8) shows bonds of OH and $\text{Mg}(\text{OH})_2$ at wave numbers above 3500 cm^{-1} which indicate the corrosive attack. Figure 9a depicts a photograph from a light-microscopy investigation of the magnesium surface where the points of attack are obvious. Comparing this picture with the allocation of polymer in the same area demonstrates clearly that the thickness of the polymer at the point of attack is very thin or the polymer is completely absent (figures 9b and c). Simultaneously the amount of $\text{Mg}(\text{OH})_2$ and water increases as presented in figure 9d.

Such defects could have already been in the coating or they are formed due to magnesium corrosion. It is observed that during immersion bubbles emerge from the surface so that a gas formation may crack the polymer layer. The reason might be the reactions of magnesium during the corrosion process as described by Song et al.[20] An electrochemical reaction causes the dissolution of Mg as Mg^{2+} which in the presence of water and H^+ ions (from dissociated water) leads to the chemical reaction:



which forms



The produced hydrogen causes increasing gas pressure underneath the polymer. The hydrogen permeability of the polymer is much lower than the reaction rate, and this leads to an excess pressure that finally ends in bursting of the polymer film. However, the reaction is initiated by failures in the polymer coating. Consequence of which is the diffusion of water and

electrolyte that allows the interaction of these with the alloy while the transport of the generated products (H_2 and $Mg(OH)_2$) is hindered. Those defects are a result of incompatibility between polymer solution and areas of the metal surface. Maybe that grain boundaries, segregations or other irregularities in the surface cause a lower wettability and therefore finally lead to uncoated areas. It seems that a special cleaning or pre-treatment process for the magnesium is necessary to obtain perfect dense and defect-free polymer coatings.

Combination of organic corrosion inhibitors and non-porous polymer coating

Pitting corrosion starts in the location of the noblest inclusions. A chemical and electrochemical dissolution of magnesium occurs at the initial steps of the corrosion process leading to dealloying of intermetallic zones. The intermetallic precipitates act as anodes and cathodes at the same time [20]. Previous investigations based on aluminium and its alloys by Lamaka et al. [21] show that organic compounds are able to play a role as inhibitors against corrosion. It is postulated that the inhibitors form a thin adsorptive protective layer on the surface of the aluminium alloy which leads to a passivation of active intermetallic zones due to the prevention of dissolution of Mg and Al. These authors used especially 8-hydroxyquinoline, salicylaldehyde and quinaldic acid for corrosion protection of aluminium and its alloys. In the present work we also used benzotriazole (BTA), which is well known as organic corrosion inhibitor.[22-25]

In the case of 8-hydroxyquinoline no dense polymer layer could be produced. Figure 10 and 11 show the EIS diagrams of the three organic inhibitors embedded in the PEI in comparison to the pure coating without any organic compound added. After 30 minutes the quinaldic acid system shows lowest impedance and the salicylaldehyde seems to be the best performing inhibitor. But all systems differ not significantly to those polymer coatings without any additive. However, during the exposure time of 84 hours in 3.5 wt.-% NaCl all systems come down to the level of self-protected magnesium alloy. The slightly increased protection behaviour of BTA could be caused by different coating thickness which was in the range of about 3 μm . As mentioned above, defects in the coating could be the reason for the unsatisfying corrosion protection of the polymer layer especially when organic inhibitors were used. Therefore, the thickness of the coating was increased by a factor of two for the salicylaldehyde system, which had been the one with the highest starting impedance in the previous tests. Figure 12 shows the degradation of this sample followed by EIS measurements. Already after 12 hours the coating was damaged and the impedance level of

the pure magnesium alloy was reached. During the remaining time no effect of self-healing or self protection could be observed. Increasing the thickness of the coating may lead to a lower mechanical stability of the polymer as it becomes more and more brittle and also loses adhesion to the metal surface. Another effect might be the lower effective gas transport of hydrogen out of the interface between polymer and metal as well as the formation of $Mg(OH)_2$. Both bursts the polymer layer irreparable.

Conclusions

Coating of magnesium and its alloys, especially AZ31, with poly(ether imides) appear to be a promising way of corrosion protection and controlling degradation. The suitable performance of porous PEI as a protection layer on magnesium AZ31 opens a wide market for many fields of application particularly for biomaterials. It is shown that the coated materials will have an excellent performance if the coating is microporous. In this case, a kind of self-protection could be observed which circumstances need further investigation. If non-porous polymer systems are used, the integrity of the metal surface is still a problem. Hydrogen gas production according to local chemical and electrochemical interactions results in damaging of the polymer layer. Future development is needed to develop advanced cleaning and pre-treatment procedures of the metal surface.

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Figures

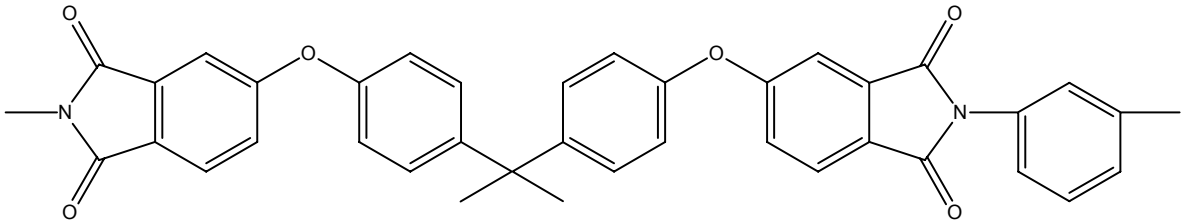


Figure 1: Chemical structure of a repetition unit of poly(ether imide) Ultem 1000[®]

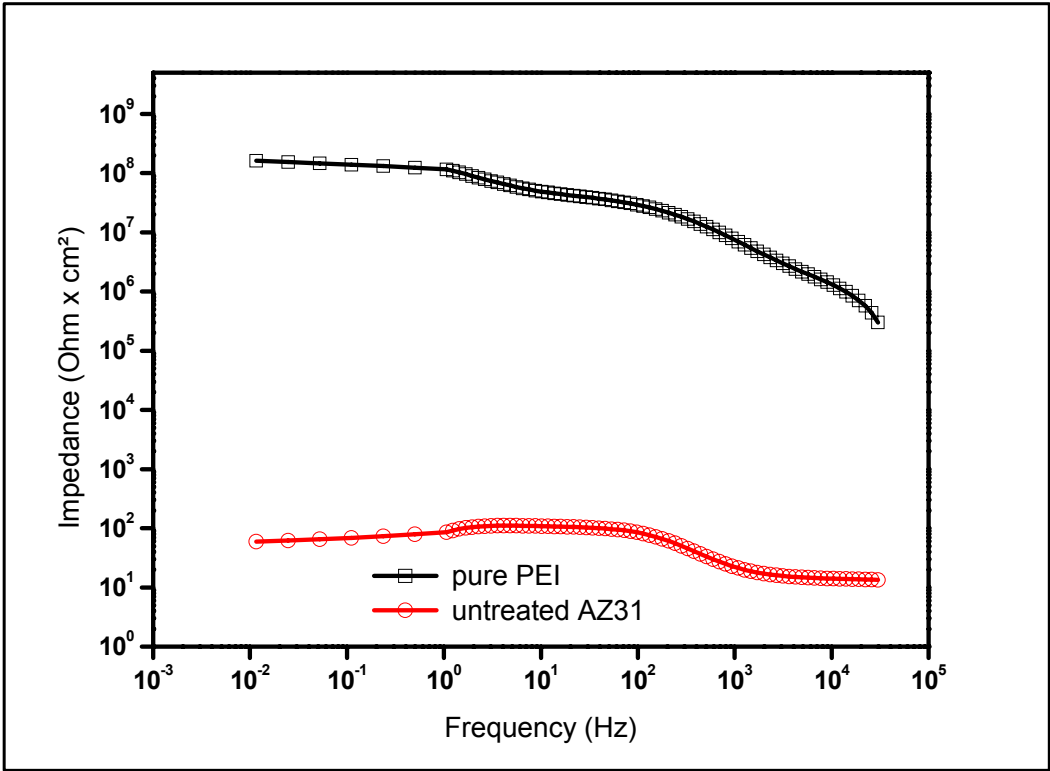


Figure 2: Bode plots of raw materials in 3.5 wt.-% NaCl (PEI after 72h, AZ31 after 30 minutes)

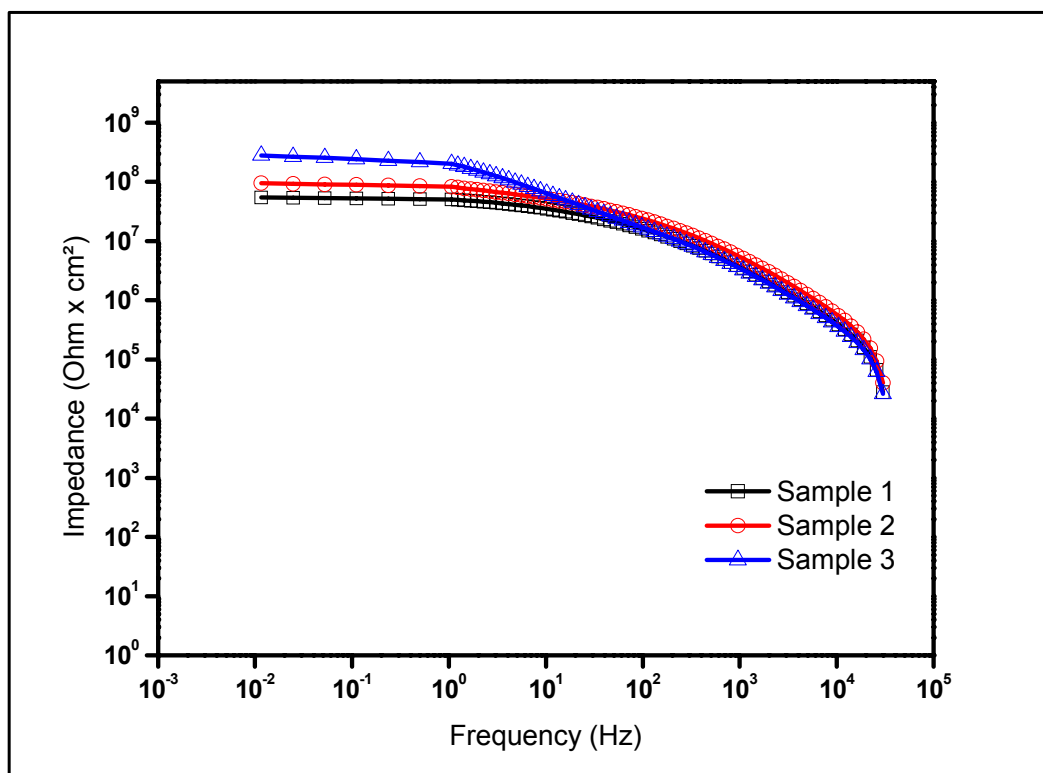


Figure 3: Bode plots demonstrating the reproducibility of porous PEI coating after 18 hours

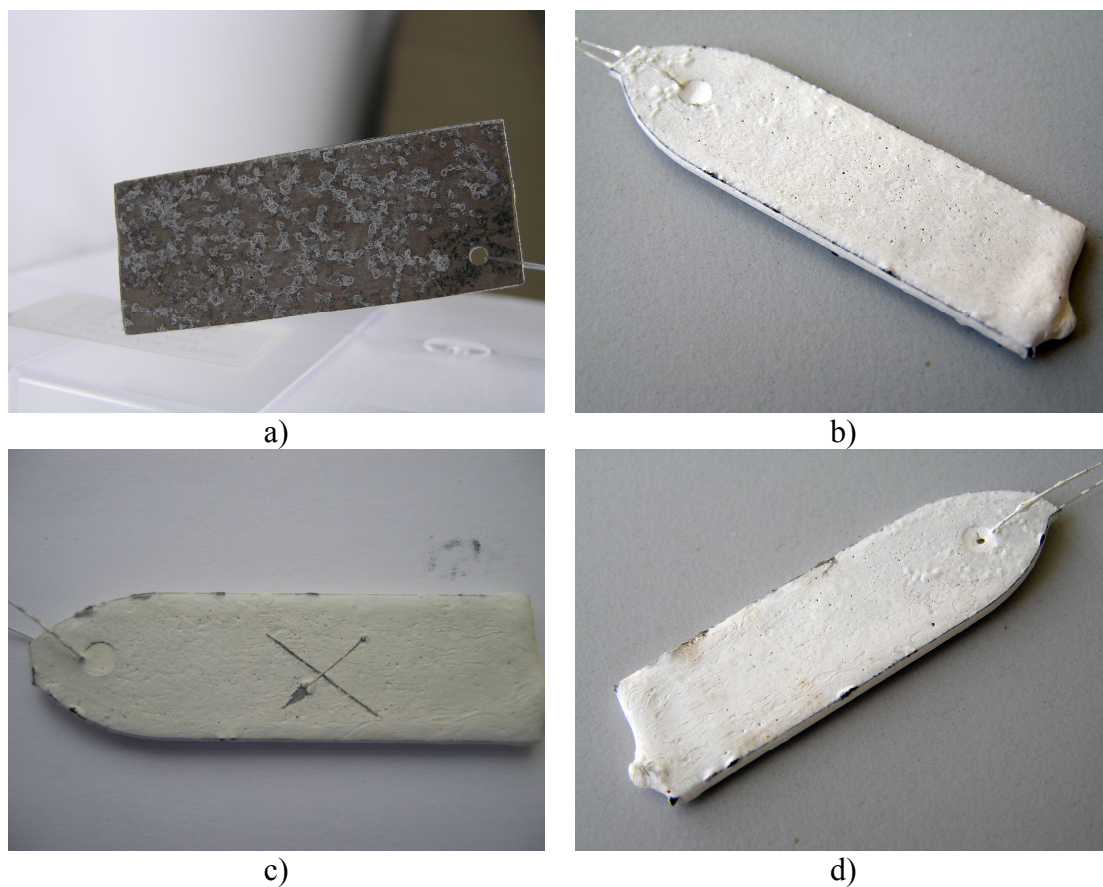


Figure 4: AZ31 specimen a) uncoated after 24 h exposure to salt spray test and coated with porous PEI b) before c) after 48 h exposure to salt spray test d) after Volvo test

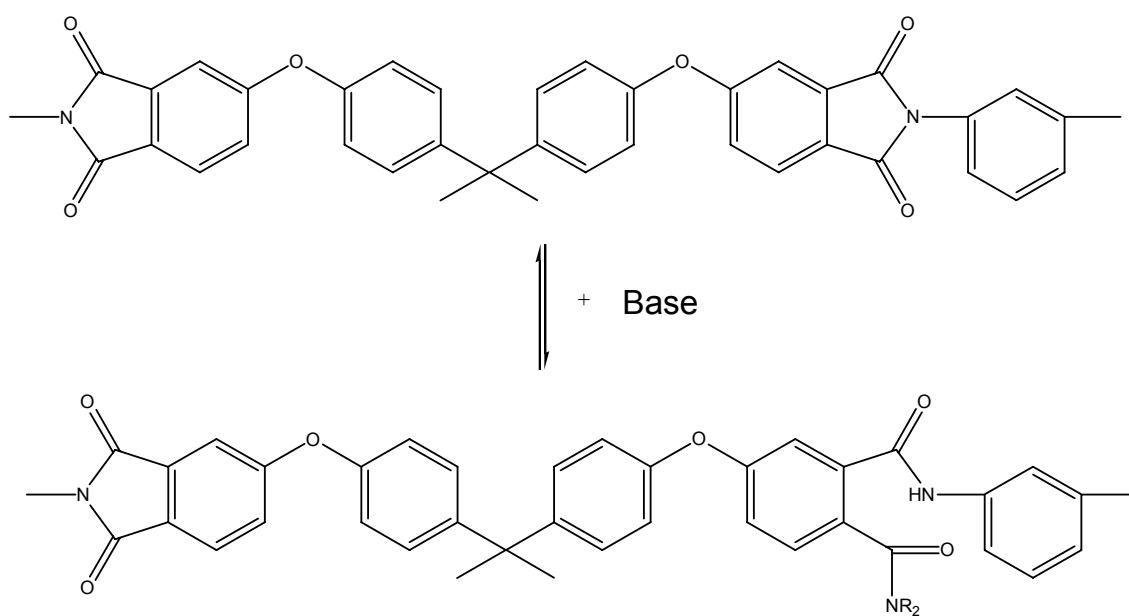


Figure 5: Opening of imide ring by interaction with a strong base

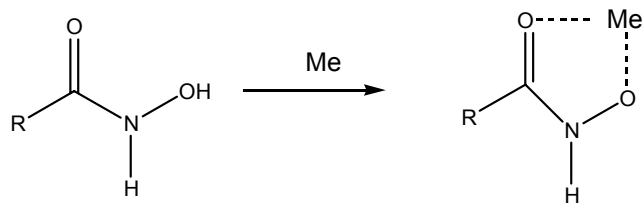


Figure 6: Coordination of metal at the anion of hydroxamic acid

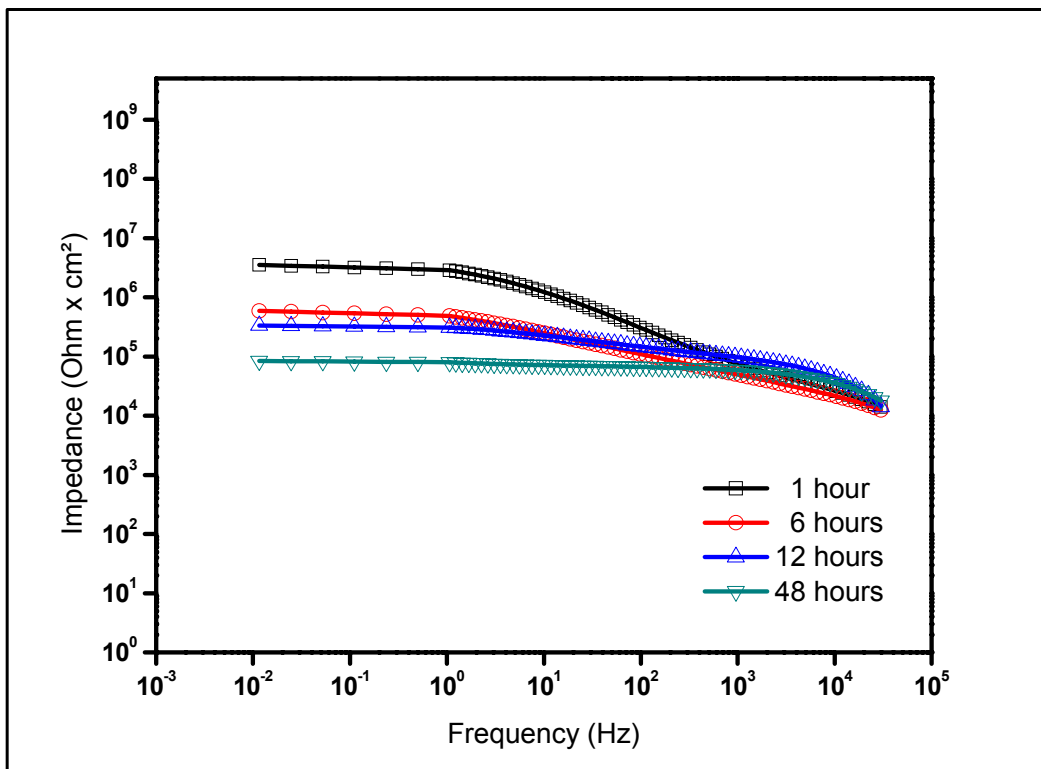


Figure 7: Bode plots revealing degradation of dense PEI coating

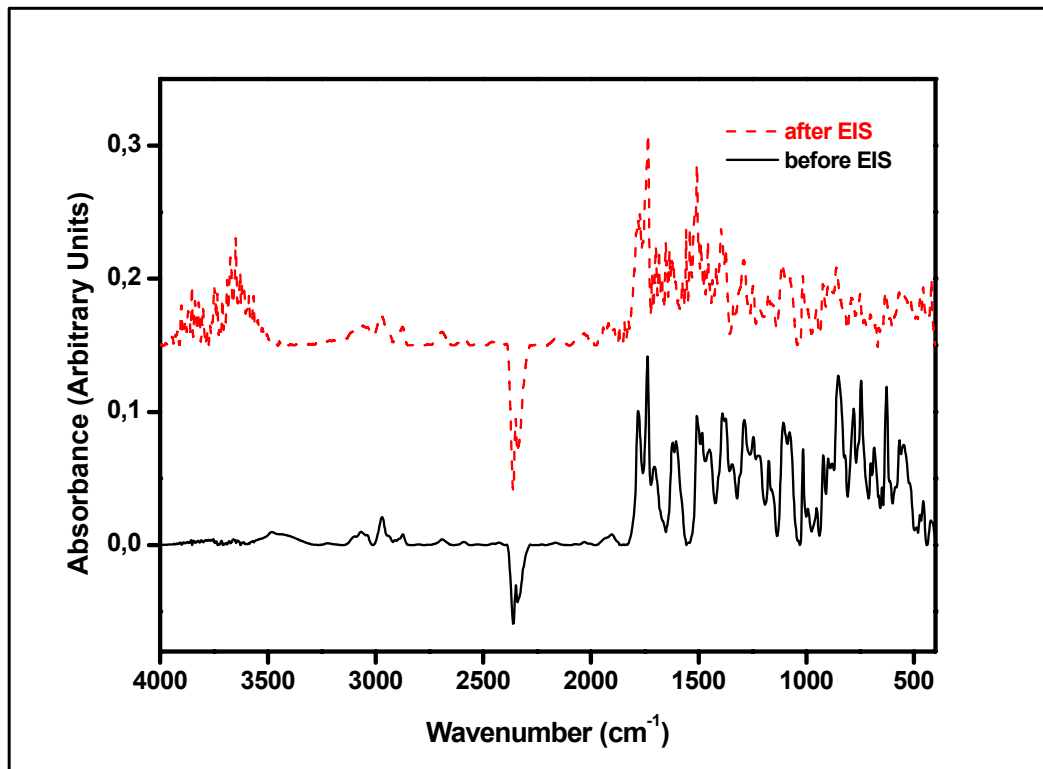


Figure 8: ATR-IR spectrum of PEI coating on AZ31 before (lower spectrum) and after EIS (upper spectrum)

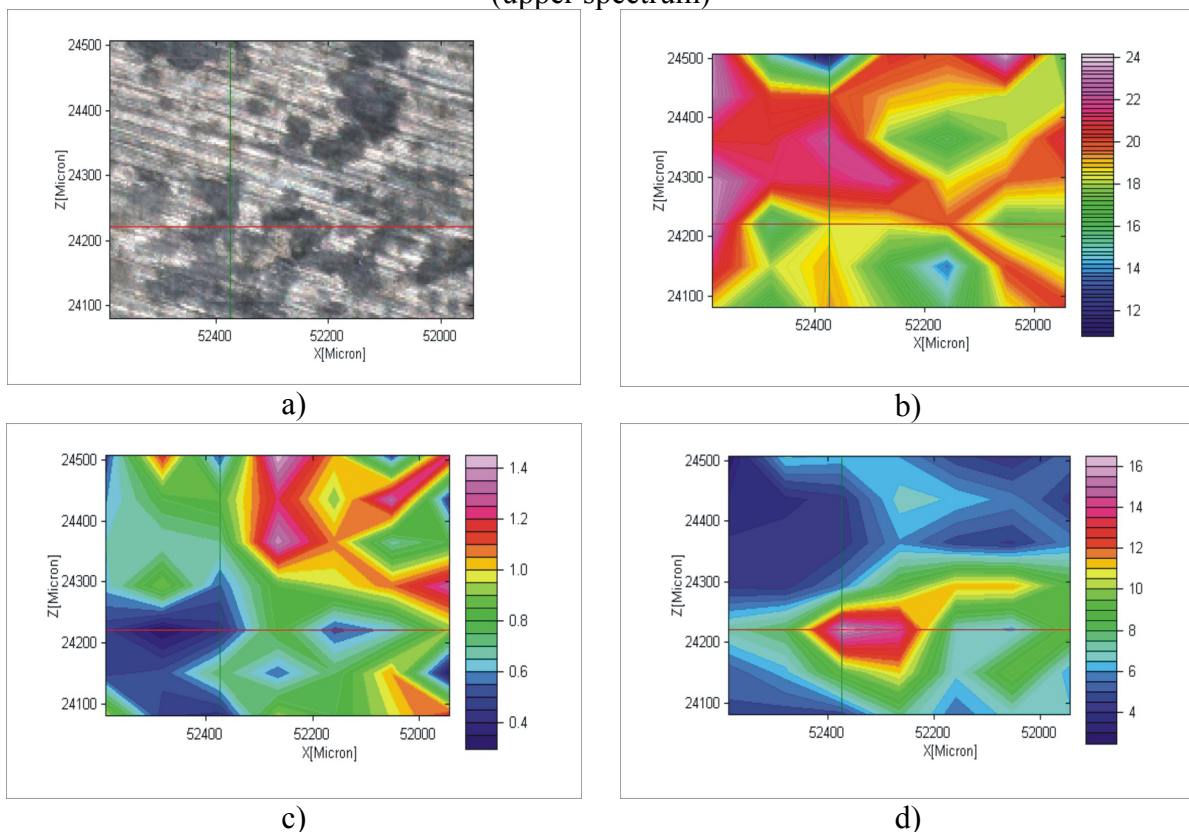


Figure 9: Surface of a dense PEI-coated AZ31 sample after EIS. **a)** light microscope 40x, **b)** ATR-IR microscope (40x) mapping of polymer distribution ($1000-1300\text{ cm}^{-1}$), **c)** ATR-IR microscope (40x) mapping of polymer distribution (aromatic region $2800-3100\text{ cm}^{-1}$); **d)** ATR-IR microscope (40x) mapping of corrosion product distribution ($\text{Mg}(\text{OH})_2$ and water (above 3500 cm^{-1}))

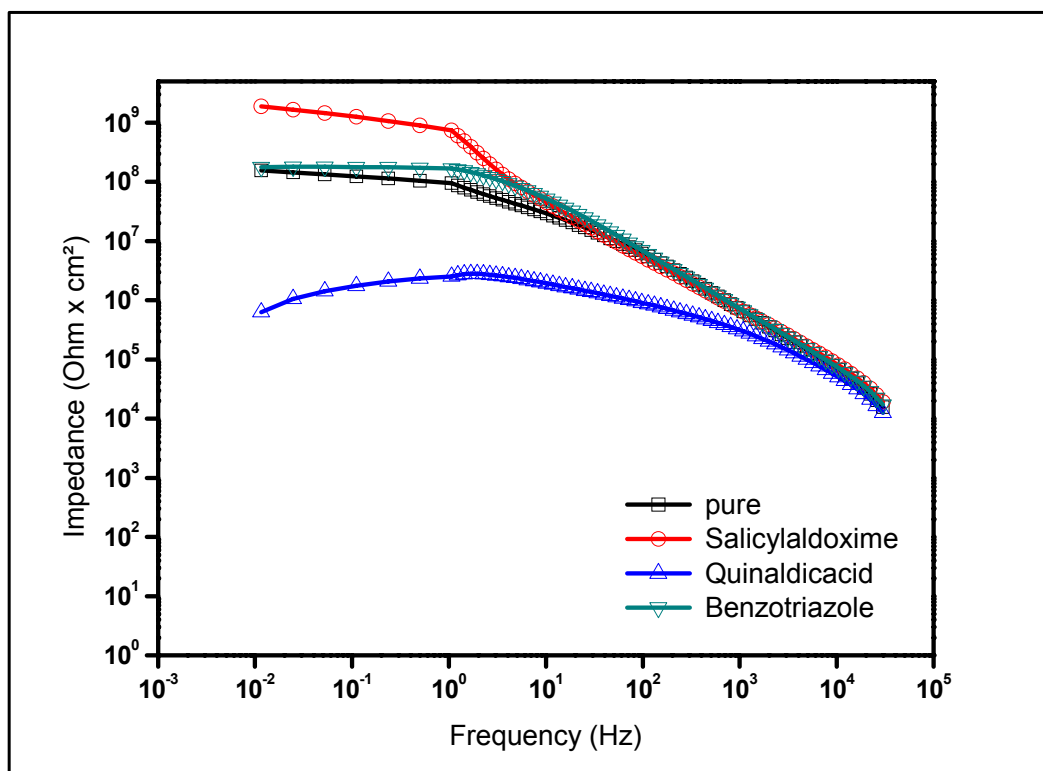


Figure 10: Bode plots of organic corrosion inhibitors embedded into dense PEI coating after 30 minutes exposure

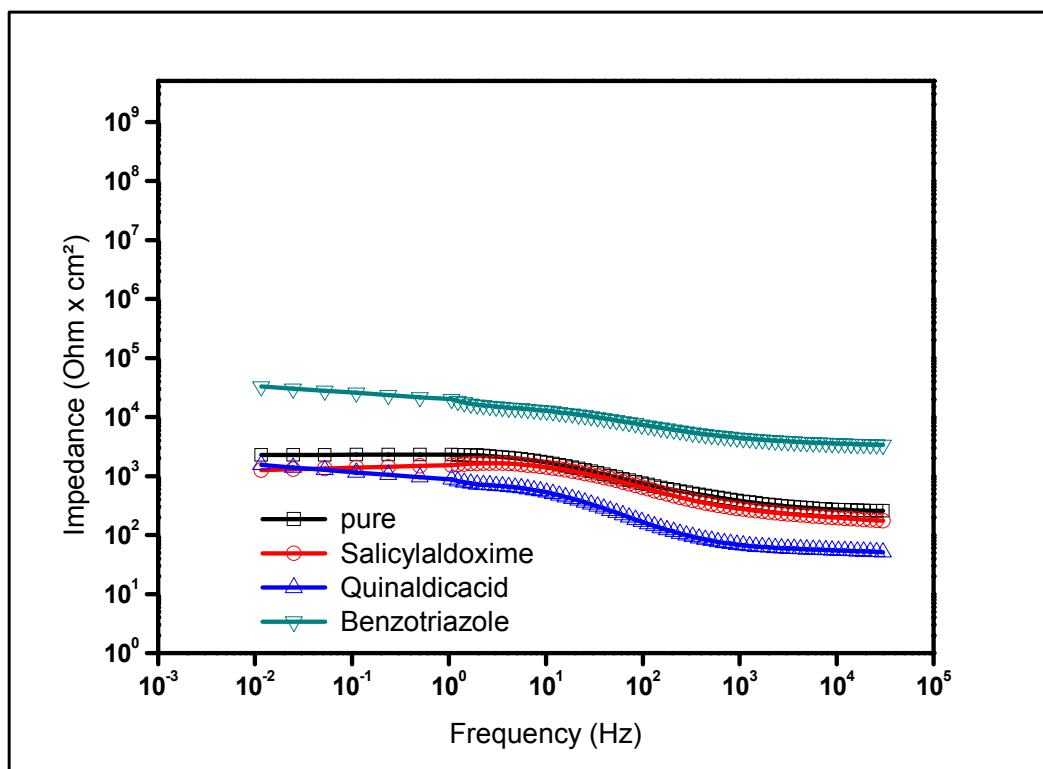


Figure 11: Bode plots of organic corrosion inhibitors incorporated into dense PEI coating after 84 hours exposure to NaCl solution

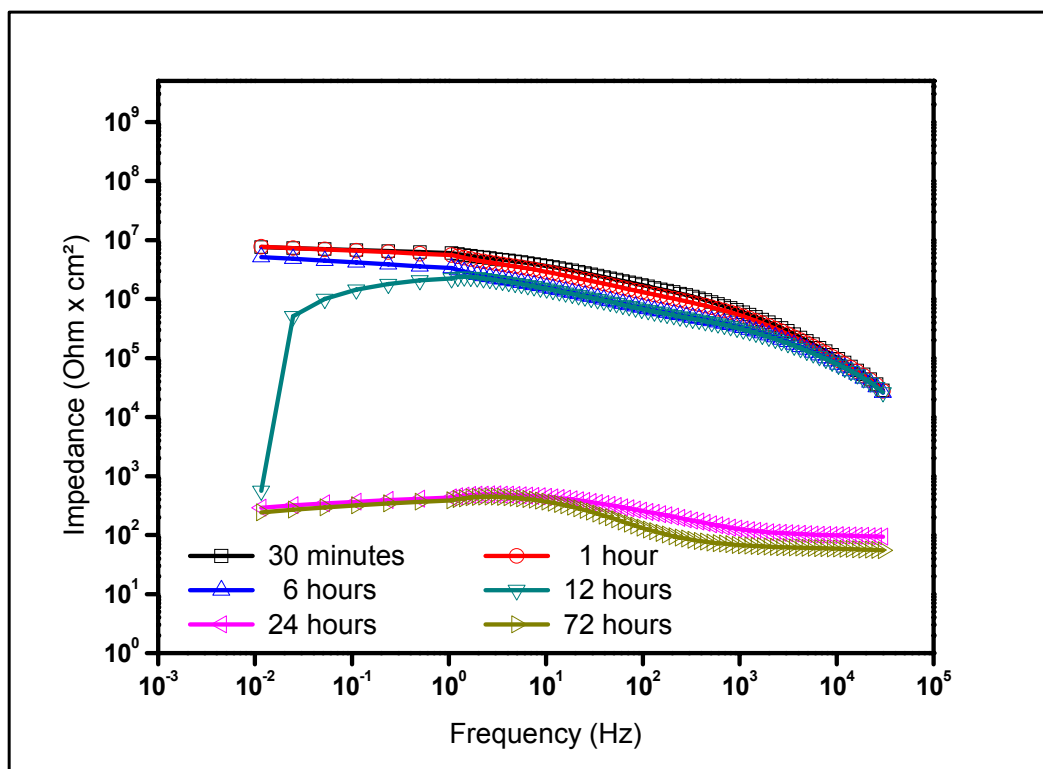


Figure 12: Bode plots of time evaluation on dense PEI coating with salicylaldehyde as organic corrosion inhibitor