



Original scientific paper

Anticorrosive polystyrene coatings modified with tannic acid on zinc and steel substrates

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Abstract

Polystyrene (PS) polymer layers were prepared by the sol-gel method and studied as anticorrosive barrier layers on carbon steel and zinc substrates. To increase the corrosion resistance of the coatings, two different approaches were considered: (i) the use of mesoporous silica-nanocontainers impregnated with a corrosion inhibitor (tannic acid) introduced into the polystyrene matrix and (ii) direct impregnation of polystyrene coatings with the same corrosion inhibitor. The impregnated nanocontainers were characterized by transmission electron microscopy. The thickness and the adhesion of the coatings were measured, and their corrosion behavior was investigated by electrochemical impedance spectroscopy. Results showed that the used inhibitor slightly decreased adhesion, but significantly increased the corrosion resistance of the coatings. The direct introduction of tannic acid into the polymer matrix offers higher corrosion resistance than in the case of polystyrene coatings doped with impregnated silica nanocontainers.

Keywords

Polystyrene coatings; corrosion protection; tannic acid; mesoporous silica nanocontainers

Introduction

Corrosion is an inevitable phenomenon in the gradual deterioration of metals because of aggressive environments and researchers are constantly preoccupied with preventing or minimizing it [1]. Methods of anticorrosion protection include the production of metal alloys (active protection) and the application of corrosion barrier layers on metals surface (passive protection). Aiming to avoid health issues and environmental problems, the production of chromate-free coatings [2] and harmless, effective organic and inorganic barrier coatings [3,4] on metals have taken the place of previously performant technologies having carcinogen nature and general toxicity [5].

Styrene, alongside a plethora of polymerizing agents forms polystyrene (PS), a vinyl polymer composed of a long hydrocarbon chain with phenyl groups attached to every other carbon atom. The most common use of polystyrene is in the production of plastics [6], and since it exhibits

interesting thermic characteristics, it is the precursor of Styrofoam, a material widely used in various industries. In the corrosion protection domain, PS has mainly been used in the form of copolymers with different acids [7] or the form of a copolymer with cornstarch [8] for the corrosion protection of steel substrates. PS microcapsules containing silanol and Ce (III) inhibitors in epoxy coatings have also been reported as corrosion barrier systems [9]. PS, as any other coating matrix offers, the possibility of improvement by the addition of corrosion inhibitors.

Reported examples of corrosion inhibitors for steel and zinc are rare earth salts (such as CeCl_3 or LaCl_3) [10], organic compounds, such as benzotriazole [11], and gallotannins [12] such as gallic acid and tannic acid, with rust converter characteristics. Tannic acid, a safe, non-toxic and environmentally friendly polyphenolic compound, forms complexes with the surfaces of the metal substrates generating an additional corrosion preventive thin film on the metallic structures [13]. These complex-forming characteristics of gallotannins, especially of tannic acid, make them eligible as inhibitors for the preparation of corrosion-resistant coatings.

Nanocontainers are widely used as corrosion inhibitor carriers in various systems. These nanoparticles offer ingenious solutions for the preparation of self-healing coatings by their versatility and the capability of controlled release of incorporated inhibitors. Previous studies discuss the application of urea-formaldehyde microcapsules filled with epoxy resin for self-healing coatings on steel substrates [14]. Mesoporous silica nanoparticles loaded with molybdate [15] or 2-mercaptobenzothiazole [16] were also reported for the corrosion protection of aluminum and steel alloys. The silica nanocontainers have also been reported in combination with tannic acid, used as a sealing agent, for benzotriazole impregnated mesoporous particles [17].

As mentioned above, applications of silica nanoparticles are widely discussed as inhibitor carriers in various coating systems. Following that thought pattern, we aimed to study whether the introduction of tannic acid in the nanocontainers *versus* the direct introduction into the coating would have a more beneficial effect on the PS coating, which by itself had a measly protective effect. Consequently, the aim of this study was the preparation of protective PS polymer coatings on zinc and steel substrates in the absence and in the presence of tannic acid as a corrosion inhibitor. The novelty of the research consists in the comparison between the characteristics of PS coatings prepared on zinc and mild steel by dip-coating, using two different approaches: (i) direct addition of tannic acid into the sol before polymerization of styrene and (ii) addition of tannic acid impregnated silica nanocontainers into the sol. The coatings were characterized by electrochemical impedance spectroscopy (EIS), the synthesized mesoporous nanocontainers were analyzed by transmission electron microscopy (TEM), and the prepared coatings were also subjected to adhesion and coating thickness measurements.

Experimental

Materials and methods

Zinc and mild steel substrates were used as metal substrates for the produced coatings. The used metal wafers were pre-treated: firstly, both metal substrates were abraded with rougher emery papers in the range of 800-1500, then polished with fine emery papers (grain size in the range of 2000-5000) followed by a degreasing step, prior to the application of the coatings.

Polystyrene sol was prepared from the 1:2 ratio of Syntevne-404 (GALLSTAFF MULTIRESINE) and Dibenzoyl peroxide 97 % (ALFA-AESAR). Mesoporous silica nanocontainers were synthesized from the mixture of tetraethyl orthosilicate (SIGMA-ALDRICH), absolute ethanol 99.9 % (SIGMA-ALDRICH), cetyltrimethylammonium bromide ≥ 98 % (SIGMA-ALDRICH), and sodium hydroxide 97 %

(ACS REAGENT). Tannic acid (SIGMA-ALDRICH), as a corrosion inhibitor, was introduced in 1 wt.%, separately into the coating matrix, respectively into the synthesized silica nanocontainers.

Protective coatings were prepared using a homemade dip-coater. Electrochemical measurements were effectuated on a AUTOLAB 302, with the use of a three-electrode cell in 0.2 g/L Na₂SO₄ (SIGMA-ALDRICH) electrolyte solution. The three-electrode cell consisted of a working electrode (zinc and mild steel substrates), a counter electrode (platinum wire) and a reference electrode (Ag/AgCl/KCl_{sat}).

TEM measurements were performed on a H-9500,100-300 kV HITACHI HIGH-TECH GLOBAL machine. Adhesion was measured with a TQC ADHESION TEST KIT while coating thickness measurements were effectuated with the use of an ELMATRONIC F / NF -1250 μm measuring instrument.

Synthesis of silica nanocontainers

0.5 ml of 2 M NaOH was added to a mixture of 0.5 g of CATB and 70 ml of water. The mixture was then heated to 80 °C and 4 mL of TEOS was added with continuous stirring. After stirring at 80 °C for two hours, an opaque, milky solution was obtained. The precipitated solution was filtered, following which the filtrate was rinsed with distilled water (2×5 mL) and ethanol (2×5 mL). After drying in an oven for approx. 24 hours, the filtration was sintered at 600 °C for 5 hours. The process leads to obtaining mesoporous silica nanocontainers.

Parts of the nanocontainers were added to an aqueous tannic acid solution, for impregnation. The nanocontainers were kept for 1 hour in the 1 wt.% tannic acid solution before being filtered and washed with both water and ethanol to remove the tannic acid from the exterior of the mesoporous silica particles.

Transmission electron microscopy measurements

Transmission electron microscopy (TEM) measurements were performed on the mesoporous silica nanocontainers with a H-9500,100-300 kV HITACHI HIGH-TECH GLOBAL measuring instrument. TEM analysis served to determine the diameter of the silica nanocontainers in order to establish whether the tannic acid molecule fits on the inside of the mesoporous silica particles.

Preparation of polystyrene precursor

Four different styrene precursor solutions were prepared. The four different solutions were based on a 1:2 mixture of styrene and its polymerizing agent, dibenzoyl peroxide. One solution was left for a polystyrene layer reference (PS); in the second, nanocontainers were added in a concentration of 1 % (PS+NC); tannic acid was added in a concentration of 1 % to the third (PS+TA), and nanocontainers impregnated with 1 % tannic acid (PS+TA+NC) were added to the last solution. In every case, following the addition of filler substances, the PS sol was placed in an ultrasonic bath for approximately 15 minutes to ensure desolvation and avoid agglomeration of the aforementioned substances. All four precursor solutions, based on preliminary studies, were allowed to polymerize for 10 days until they reached the optimum viscosity for layer drawing.

Preparation of coatings on zinc and mild steel substrates

For both metal substrates, the same pretreatment steps were followed: the first step of the pretreatment was the sanding, followed by the degreasing of the metal wafers. The zinc plates were polished using a polishing machine and an organic-based polishing paste, then degreased in hydrochloric acid, rinsed with distilled water, sonicated in alcohol, and finally dried. In the case of mild steel sheets, as they proved to be more delicate to treatment with hydrochloric acid, the

surfaces were first sanded with coarser sandpaper, then thoroughly washed with a detergent containing caustic soda, in order to get the pre-existing paraffin coating, of the mild steel, off. Mild steel sheets were then rinsed in alcohol and dried in a manner similar to the zinc substrates.

The layers were applied to the metal surfaces by the dip-coating method. Two samples were prepared from each of the four sols to monitor reproducibility. The layers were drawn at a rate of 12 cm min^{-1} . After layer drawing, thermal treatment at $80 \text{ }^\circ\text{C}$ for one hour was applied until the polymerization process was complete. The end of the polymerization was indicated by the hardening of the layer.

Adhesion and layer thickness measurements

The adhesion measurements were performed with a robust grating cutter with an aluminum head, with replaceable blades called a TQC ADHESION TEST KIT. The cutter had self-aligning blades that followed the line of the surface. A symmetrical square mesh was scratched into the metal substrate. Subsequently, a special adhesive tape meeting international standards was placed on the scratched surface of the plate. The number of incised squares remaining intact on the surface versus the number of squares that ripped off with the tape came up with the tape, the percentage of adhesion was calculated using the Lattice-Notch formula according to certain standard tables.

The layer thickness was determined using an instrument that is able to read coating thicknesses on both metallic and non-metallic surfaces by magnetic induction or eddy current method for layers of any origin, namely an ELMATRONIC F / NF -1250 μm measuring instrument. Placing the apparatus perpendicular to the layered metal surface, layer thickness values for each of our different types of layers were determined.

Wettability measurements

Wettability measurements were carried out by the sessile-drop method on all substrates and coatings mentioned. The measurements were made by adding a $20 \mu\text{l}$ electrolyte droplet of 0.2 g/L Na_2SO_4 electrolyte solution of pH 5, in a saturated Na_2SO_4 vapor atmosphere. The resulting images were processed, and contact angle determination was made in ImageJ software (developed by Wayne Rasband).

Electrochemical characterization of the coatings

Electrochemical measurements were performed on a PARSTAT 227 potentiostat, using a three-electrode cell consisting of a working electrode (zinc and mild steel wafer), counter electrode (Pt wire) and a reference electrode ($\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$) immersed in 0.2 g/L sodium sulphate (SIGMA-ALDRICH) (pH 5) electrolyte solution. The layers were firstly characterized by open-circuit potential measurements (OCP) in order to determine the resting potential values of both the coated zinc and mild steel samples. OCP measurements were left to stabilize for 60 minutes each and offered a benchmark for all further electrochemical characterization.

In a further study, electrochemical impedance spectroscopy (EIS) measurements were performed in the 10 mHz to 100 kHz frequency range with the use of a sinusoidal current (10 mV).

Results and discussion

Transmission electron microscopy analysis

Previously prepared silica nanocontainers were subjected to TEM analysis and the obtained images are shown in Figure 1. The purpose was to get information about the shape and diameter of the particles and to determine if they belonged to the nano range at all. Furthermore, we also

wanted to know whether the inhibitor molecule, more specifically the tannic acid molecule fits in, given that it is a molecule of 1.85×1.65×1.01 nm [18]. Based on the TEM images, we can state without any doubt that the diameter of the nanocontainers is in size range of 20 to 50 nm. This would theoretically allow the tannic acid molecule to be hosted by the nanoparticles.

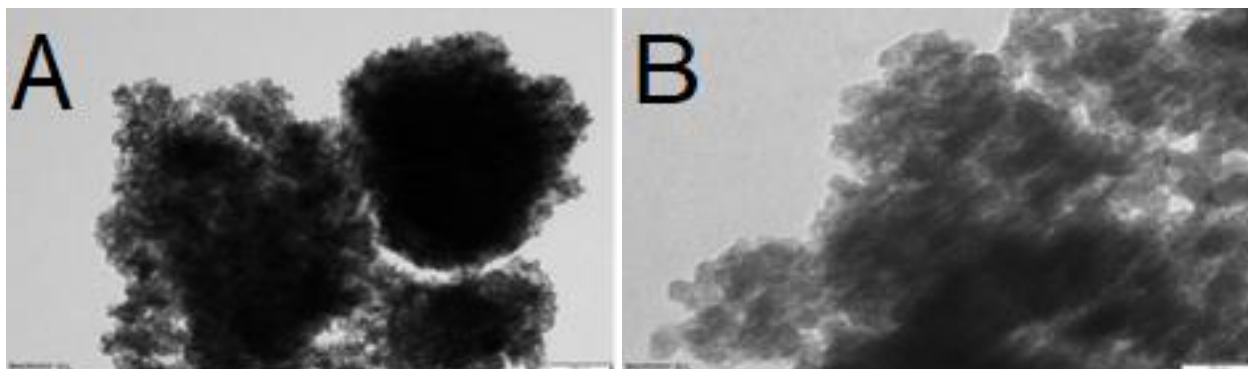


Figure 1. Transmission electron microscopy images reflecting a cluster of synthesised mesoporous silica nanocontainers at scales of (A) 200 nm respectively (B) 50 nm

Adhesion and coating thickness evaluation

Prior to the application of the PS-based layers and the measurement of their adhesion to the substrate, the surface of the plates was subjected to thorough cleaning and polishing operations. All these procedures were required in order to presumably promote a high level of adhesion of the protective coating. The purpose of measuring the adhesion was to obtain information about the quality of a protective coating, more precisely, how and to what extent it has established a high-quality, long-lasting adhesion to the sheet to be protected. If adhesion proves inadequate, electrolyte infiltrations may occur beneath the layer, which can cause local corrosion, which is worse than corrosion that occurs in the complete absence of a protective coating.

Adhesion was quantified by coating type since there were no observed significant differences between the adhesion of the coatings on the two different metals. To calculate the adherence of the prepared coating types, the Lattice-Notch equation (1) was applied. In Equation 1, the parameter a stand for the total of squares meshed into the coating, while b , for the total number of squares ripped off by the special tape. Adhesion can parallelly be assessed with the help of so-called ASTM standards [19], which also take into consideration the measure by which the coating gets damaged following the tearing of the square mesh. These standards come as follows: 5B (no detachment), 4B (detachment of flakes, a maximum of 5 % damage), 3B (coating flaking around the edges, less than 15 % damage), 2B (detachment of ribbons with the cuts and squares, damage less than 35 %), 1B (greater detachment of the coating along the cuts, part of the squares gone, damage lesser than 65 %) and 0B (flaking that cannot be classified).

$$\text{Adhesion} = \frac{a-b}{a} 100 \quad (1)$$

It can be observed from Table 1 and Figure 2 that the presence of tannic acid, although slightly reduces adhesion for both substrate types.

The obtained adhesion results can be explained by the fact that the formation of metal tannates on the metal surface by a reaction between TA and the metal is a faster process than the polymerization of polystyrene. If so, the polystyrene adheres to an intermediate porous layer formed by a complex of iron or zinc oxides and tannic acid [13], which leads to poorer adhesion.

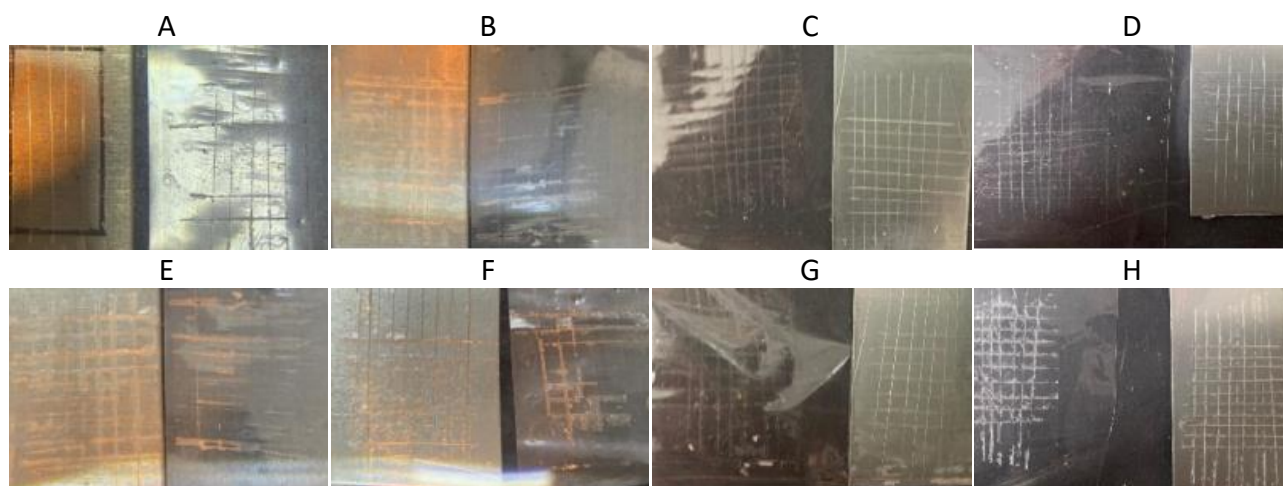


Figure 2. Adhesion tests performed on both mild steel and zinc substrates coated with the following layers: (A) Zn PS, (B) Zn PS+NC, (C) Zn PS+TA, (D) Zn PS+TA+NC, (E) mild steel PS, (F) mild steel PS+NC, (G) mild steel PS+TA, (H) mild steel PS+TA+NC

The layers thicknesses were determined for all the investigated coatings using an instrument that is able to read layer thicknesses on surfaces by magnetic induction or the eddy current method. The results are presented in Table 1 and show that the addition of NC or TA in the PS layer leads to an increase of the coating thickness, which is approximately the same in all cases, around 20 μm .

Table 1. Results of adhesion and layer thickness evaluation for the PS, PS+NC, PS+TA and PS+TA+NC coatings on zinc and mild steel substrates

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

In the case of the mild steel wafers, the coatings tore to a much greater extent, which led to the conclusion of a poorer adhesion than in the case of the zinc substrates. An explanation of this phenomenon can be that the mild steel has proven over the course of the experiment to be much more reactive to any corrosive factor than zinc, which possibly includes the additives of the PS.

Wettability measurements

Wettability measurements were performed on all types of coatings on both zinc and mild steel substrates. Figure 2 contains the results of wettability measurements and the initial contact angle values of each coating on both zinc and mild steel substrates. Tannin acid is a plant-derived polyphenolic substance that is hydrophilic, which explains the lower contact angle noticed in its presence in the coatings.

Same observation for the silica NC, which also increase hydrophilicity of the coating and thus, wettability. Nevertheless, the decrease is not a significant one.

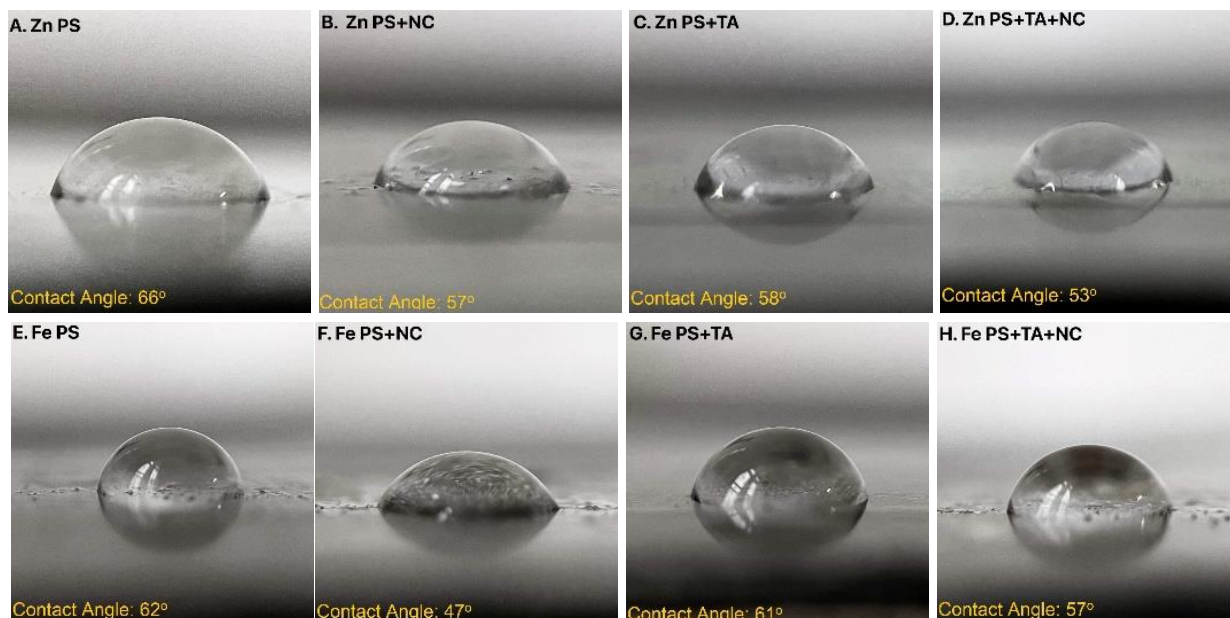


Figure 3. Wettability measurements (at 0 min) effectuated with 20 μ l droplet of 0.2 g/L Na_2SO_4 electrolyte solution on the following coatings: **A.** Zn PS, **B.** Zn PS+NC, **C.** Zn PS+TA, **D.** Zn PS+TA+NC, **E.** Fe PS, **F.** Fe PS+NC, **G.** Fe PS+TA, **H.** Fe PS+TA+NC

Electrochemical characterization

Figure 4 shows the complex plane representation of the EIS spectra of the various layers deposited on zinc plates. As expected, the impedance value of the undoped polystyrene layer (PS) on zinc is higher than the impedance of the bare zinc plate. The presence of the empty silica nanocontainers in the polymeric coating (PS + NC) ruins the impedance of the PS by lowering its impedance values beneath those of the bare zinc plate. The nanoparticles seem to act as defects of the coating, favoring corrosion. Low compatibility between PS and silica can also explain the poor corrosion resistance of (PS+NC) coatings.

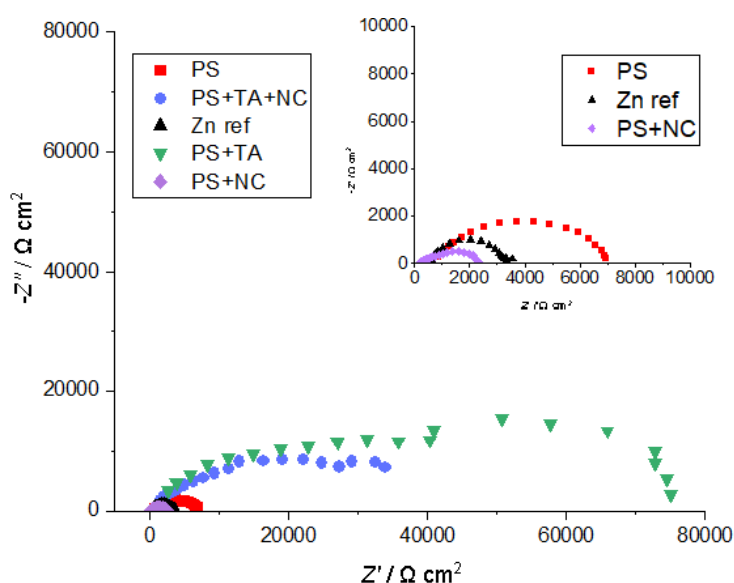


Figure 4. EIS plots of the Zn ref, PS, PS+NC, PS+TA, PS+TA+NC coatings on Zn substrates in 0.2 g/l Na_2SO_4 solution (pH 5)

In the next step, silica nanocontainers impregnated with tannic acid were introduced into the polystyrene layer resulting (PS + NC + TA) coatings, and on the other hand, PS coatings were directly impregnated with tannic acid (PS+TA).

The EIS plots corresponding to the different coatings put in evidence the beneficial effect of tannic acid. Tannic acid is known as an effective anticorrosive agent [20] that reacts with corrosion products formed on the metal surface and stabilizes them. This characteristic can be observed in this case as well.

A comparison between the impedance spectra of Zn/(PS + NC +TA) and Zn/(PS+TA) coatings leads to the conclusion that TA is more effective when it is directly incorporated in PS (a larger capacitive loop is observed in the latter case). This is probably due to the fact that tannic acid is likely to remain adsorbed in a higher concentration in PS than in the presence of nanocontainers, which were washed with water after impregnation and some tannic acid may have been removed during the process. A second possibility is the better compatibility between PS and TA than between PS and silica. Compared to the PS and (PS + NC) layers, tannic acid strongly exerted an inhibiting effect both in the (PS + TA + NC) and the (PS + TA) coatings. It can also be observed that in the presence of TA in the coatings, the shape of the spectra changes (a second capacitive loop is outlined), suggesting the change in the mechanism of the corrosion process. Further research and modelling of the spectra will elucidate this aspect.

Figure 5 presents the impedance spectra of coatings deposited on mild steel substrates coated with the same aforementioned sols.

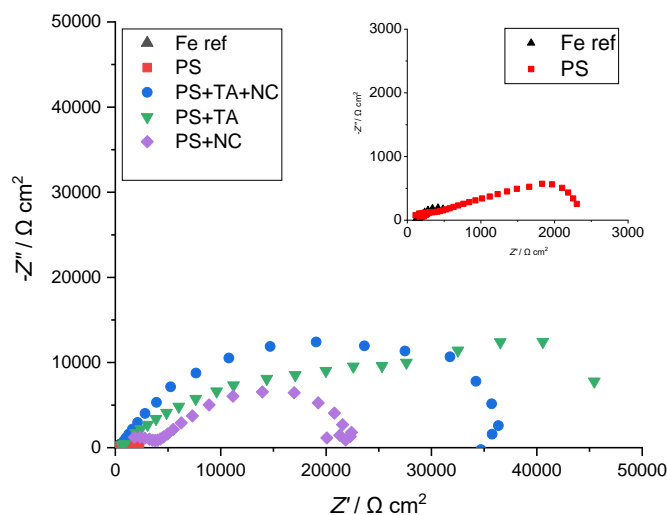


Figure 5. EIS plots of the Fe ref, PS, PS+NC, PS+TA, PS+TA+NC coatings on mild steel substrates in 0.2 g/l Na_2SO_4 solution (pH 5)

The same resistance-improving effect of tannic acid, either embedded in silica nanocontainers or directly in the polymeric matrix, was observed compared to the undoped PS coating. At the same time, it should be mentioned that compared to the modified PS layers on zinc, the (PS+TA) and (PS+NC+TA) layers drawn on mild steel show lower impedance values.

This observation was corroborated with literature data mentioning that tannic acid is a more efficient inhibitor on zinc than on mild steel [20]. A possible explanation in our case could be the fact that zinc substrates were much easier to polish in the pretreatment step, resulting in a smoother surface for the polymeric coating to adhere to. In many cases, zinc has better compatibility with materials, while mild steel oxidizes extremely quickly and often forms complexes not compatible with passive corrosion protective methods.

On the mild steel substrates, the end result is the same as in the case of zinc: TA improves the corrosion resistance of the coatings, and the polystyrene layer impregnated directly with tannic acid has a higher anticorrosion resistance than that containing the TA modified silica nanocontainers.

Conclusions

The effect of tannic acid embedded in polystyrene coatings by two different ways on the anticorrosion protection of zinc and steel was investigated by electrochemical, layer thickness and adhesion measurements. On the one hand, silica nanocontainers of 20-50 μm diameter were impregnated with an aqueous solution of tannic acid, then introduced into a polystyrene coating matrix, and on the other hand, tannic acid was directly introduced into the polystyrene coating in the sol-preparation step. The results corresponding to doped polystyrene were compared with those for simple polystyrene coating and polystyrene containing empty silica nanocontainers.

Tannic acid showed an inhibitory effect in both systems compared to polystyrene layers with empty nanocontainers for zinc and steel. Unfortunately, adhesion is reduced by the presence of tannic acid. This may be due to the fact that the formation of the tannate complex on the surface determines polystyrene to bind to an intermediate, porous layer, resulting in poor adhesion of PS coatings. However, the increased corrosion resistance makes doped PS layers promising candidates for low-cost, corrosion-resistant protective coatings.

Best corrosion-resistant properties were evident when tannic acid was directly introduced into the polystyrene coating in the sol-preparation step.

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