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Corrosion resistance of hybrid films applied on tin plate: Precursor solution acidified with nitric acid (pH=3)

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Abstract
Siloxane – poly (methylmethacrylate)-based materials are systems formed by a silicon network, to which chains of poly (methylmethacrylate) are linked by covalent bonds or by physical interactions. Their stability and adherence allow their application on substrates like tin plate in order to increase the corrosion resistance. The aim of this work is to coat tin plate with a hybrid film obtained from a sol consisting of alkoxide precursors: 3 - (trimethoxysilylpropyl) methacrylate (TMSM) and poly (methyl methacrylate) PMMA. Effect of tetraethoxysilane (TEOS) addition was evaluated. Morphology was evaluated by SEM and contact angle. Electrochemical behavior was evaluated by open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Results showed that siloxane-PMMA film obtained with a higher addition of TEOS had higher thickness. However, intense densification caused by TEOS addition promoted crack formation, thereby compromising the corrosion resistance.

Keywords: Hybrid films; nitric acid; tin plate; pH=3; TEOS; corrosion.

Resistencia a la corrosión de películas híbridas sobre láminas de estaño: Solución precursora acidificada con ácido nítrico (pH=3)

Resume
Los materiales híbridos a base de siloxano y PMMA se constituyen por una red de silicona, a la que están enlazadas cadenas de polimetilmetacrilato. Su estabilidad y adherencia permiten su aplicación en láminas de estaño para aumentar la resistencia a la corrosión. En este trabajo se recubrió una lámina de estaño con una película híbrida a partir de un sol que consta de los precursores alcóxidos: 3-trimetoxisililpropilmetacrilato (TMSM) y polimetilmetacrilado (PMMA). Se evaluó la influencia de la adición de tetraetoxisilano (TEOS). Se evaluó la morfología de los filmes por SEM y ángulo de contacto. Se evaluó el comportamiento electroquímico con medidas de potencial a circuito abierto, polarización potenciodinámica e impedancia electroquímica. Los resultados muestran que la película con mayor adición de TEOS tuvo mayor espesor; sin embargo, el TEOS intensificó la densificación. Así, se formaron grietas que comprometieron la resistencia a la corrosión.

Palabra clave: Películas híbridas, ácido nítrico, láminas de estaño, pH = 3; TEOS corrosión.

1. Introduction

During the last years, polymeric-based surface treatments have arisen as non-toxic alternatives to traditional chromating process. Among those alternatives, pretreatments based on siloxane-PMMA have showed promising results, attracting attention of industries. These hybrids films improve corrosion resistance [1] and adhesion properties of organic layers. Besides, these hybrids films reduce the environmental impacts compared to the chromatization process [2]. Moreover, siloxane-PMMA hybrid films promote an excellent anchorage on the metallic surface of tin plate [3,4] for posterior paint application, which can be done by the releasing of silicone from functional siloxanes using an ultraviolet cure [5].

PMMA-based materials, such as polymeric blend [6,7]

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and organic-inorganic hybrid materials [3,8,9,10,11] have been investigated intending to get better properties. These materials are classified according to their chemical bond characteristics. Class I hybrids have their organic and inorganic components bonded by Van der Waals forces, such as PMMA on ZrO_2 [9]. Class II hybrids are created by merging the inorganic and organic phases by covalent bonds, like those obtained through sol-gel method using TMSM and TEOS as precursors [11]. These formulations combine the hardness, scratch resistance and thermal stability of the ceramic component with flexibility, transparency and tunable adhesion of the organic substances. Class III hybrids, basically consist of merging class I with class II hybrids, getting the adhesion properties of one with the inorganic-organic network provided by the other. This way, the strategy used for researchers is to employ a coupling agent such as trialkoxides silane functionalized with vinylic ligands, which allow the connexion between organic and inorganic phases [12,13,14]. A trialkoxide silane widely used a coupling agent is 3-methacriloxi-propyl-trimethoxy-silane (TMSM, also known as MPTS). TMSM, besides being a great coupling agent between organic and inorganic phases, it is photo sensitive to UV radiation, which makes it possible to control its refractive index, as in optical devices and in materials with low dielectric constant [15,16,17]. TMSM can promote the formation of uncracked, micrometric films. Also the film refractive index can be controlled by the methacrylate introduction in the hybrid structure and the curing method, such as UV or heat treatment [18] or by heat treatments, allow the increase of the refractive index.

The aim of this work is to study the behavior of hybrid films and the effect of the addition of tetraethoxysilane (TEOS) on corrosion on a tin plate substrate. The tin plate was coated with a hybrid film obtained from a sol constituted by the alkoxide precursors: 3 - (trimetoxisililpropil) methacrylate (TMSM) and poly (methyl methacrylate) PMMA, and it was evaluated the effect of the addition of tetraethoxysilane (TEOS). The films were obtained by a dip-coating process and cured for 3 hours at 160 °C. The hydrolysis was carried out at pH=3 using nitric acid.

2. Experimental Method

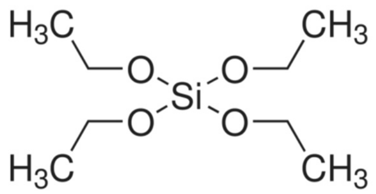
2.1. Substrate treatment

The tin plates were rinsed with acetone and dried. After that, they were degreased with neutral detergent at 70 °C by immersion for 10 minutes. Then, they were properly washed and dried.

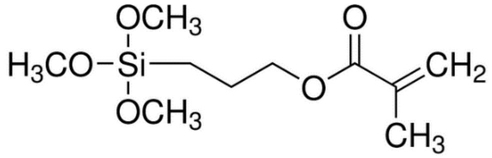
2.2. Elaboration of Siloxane-PMMA hybrid films

The hybrid films were obtained on a tin plate substrate from a sol constituted by the silane precursors: γ-methacryloxypropyl-trimethoxysilane (TMSPMA – $C_{10}H_{20}O_5Si$) and tetraethoxysilane (TEOS - $C_8H_{20}O_4Si$) with addition of methyl methacrylate (MMA), which was distilled to remove the polymerization inhibitor (hydroquinone) and impurities, and stored in a freezer prior to use. Benzoyl peroxide, BPO (reagent), was recrystallized from ethyl alcohol. The structural formula of the organic and inorganic precursors are shown in Figure 1.

Tetraethyl orthosilicate (TEOS)



3-(trimethoxysilylpropyl) methacrylate (TMSM)



Methyl methacrylate (MMA)

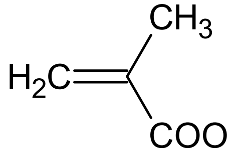


Figure 1. Structural formula of the organic and inorganic precursors. Source: Adapted from Kunst, S. R .et al 2014.

The sol-gel method was employed in the preparation of hybrid organic-inorganic materials. In the synthesis of the inorganic phase, precursors TMSM and TEOS were mixed at 60 °C for 1 hour. Hydrolysis was performed at medium pH=3 using nitric acid as a catalyst and ethanol and water as solvents. The organic phase consisted of homogenization of MMA at room temperature, where the thermal initiator was benzoyl peroxide (BPO). Finally, the two solutions (inorganic and organic) were mixed. The films were obtained by a dip-coating process, with a removal rate of 14 cm.min^{-1}. Subsequently, the coated substrates were heat treated (cured) at a temperature of 160 °C for 3 hours at a heating rate of 5 °C.min^{-1}. This treatment increases the degree of polymerization because it promotes the formation of free radicals from the C=C bonds existing in TMSM and MMA. Table 1 shows the description of samples used.

Table 1. Description of the samples.

Samples	Description
Tin plate	Tin plate without coating
T1N3	Tin plate coated with hybrid film with addition of TEOS (level 1), nitric acid and pH=3 de TEOS.
T2N3	Tin plate coated with hybrid film with addition of TEOS (level 2, increased concentration of TEOS in the level 1), and nitric acid pH=3
T3N3	Tin plate coated with hybrid film with addition of TEOS (level 3, increased concentration of TEOS in the level 1 and level 2), and nitric acid pH=3

Source: The authors.

Samples containing a small amount of TEOS in the hybrid film were named level 1, while the samples containing high amount to TEOS were named level 2 and the sample that has the greatest amount of TEOS was named level 3.

2.3. Characterization of Siloxane-PMMA hybrid films

In order to evaluate the films morphology, scanning electron microscopy (SEM) and the sessile drop method were performed.

Scanning electron microscopy (SEM) in a JEOL-JSM 5800 with an acceleration voltage of 20 keV was used to evaluate the thickness, by cross section, and the morphology of hybrid films.

The film hydrophobicity was determined by the contact angle measurement from the sessile drop method in equipment developed by the research laboratory in corrosion (LAPEC) of UFRGS. The contact angle was determined by using image analyses software (also developed by this laboratory).

The corrosion performance of the films was evaluated by the following electrochemical techniques: open circuit potential (OCP) monitoring, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements in a 0.05M NaCl solution. For the electrochemical characterization, a three-electrode cell was used, with platinum as the counter electrode and SCE (Saturated Calomel Electrode) as the reference electrode. The work electrode area was 0.626 cm². The OCP monitoring and potenciodynamic polarization curves were performed in a potentiostat PAR 273, following the ASTM G5 [19] standard. The OCP was monitored for the first hour of immersion in the electrolyte before the polarization curves and the EIS measurements. The polarization curves were measured with a scan rate of 1 mV.s^{-1} in a range from 200 mV (under OCP) up to 400 mV (above OCP). Potentiodynamic polarization was carried out in the same PAR 273 as the OCP measurements. The equipment used for the EIS measurements was a potentiostat (Omnimetra Mod. PG-05) coupled to a frequency response analyzer model Solartron 1255. The amplitude of the EIS perturbation signal was 10 mV, and the frequency range studied was from 1 x 10^{5} to 1 x 10^{-2} Hz, according to the ASTM G106 [20] standard.

3. Results and discussion

3.1. Morphological characterization

Figure 2 shows the SEM micrographs for the films studied: T1N3 (with TEOS addition of level 1), T2N3 (with TEOS addition of level 2) and T3N3 (with TEOS addition of level 3). From the SEM micrographs one can observe that the sample T1N3 (Figure 2-a) showed small discontinuities in the coating while for the sample T2N3 (Figure 2-b), the formation of the discontinuities were more accentuated. The sample T3N3 (Figure 2-c) showed cracks and delamination of the hybrid film. This is due to the formation of a complete porous ceramic structure, which is brittle [21], after hydrolysis and cross-linking of TEOS. Therefore, the TEOS addition contributed to the irregular coverage observed.

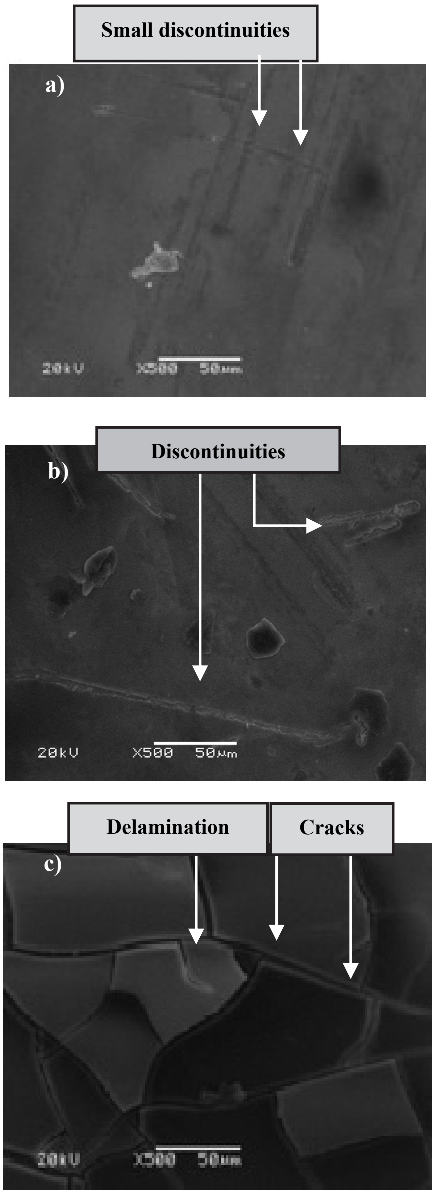


Figure 2. Micrographs obtained from SEM of hybrid films: (a) T1N3, (b) T2N3 and (c) T3N3.
Source: The authors.

The thickness of the films was determined by the analysis of images obtained by SEM of the cross section (Figure 3) and the results are shown in

Table 2. It is observed that the sample with highest thickness was the sample with greater addition of TEOS (T2N3 and T3N3), (Figure 3-b and 3-c). This is associated with higher content of silanol groups (the inorganic phase) due to the greater amount of TEOS in the film. The real density of hybrid siloxane-PMMA increases with siloxane content in the film, because the siloxane phase density (2.2 g.cm^{3}) is higher than the PMMA density (1.2 g.cm^{3}). However, it was verified that the sample T3N3 (Fig. 2-c) showed cracks due to intense densification of the film promoted by the excessive addition of TEOS.

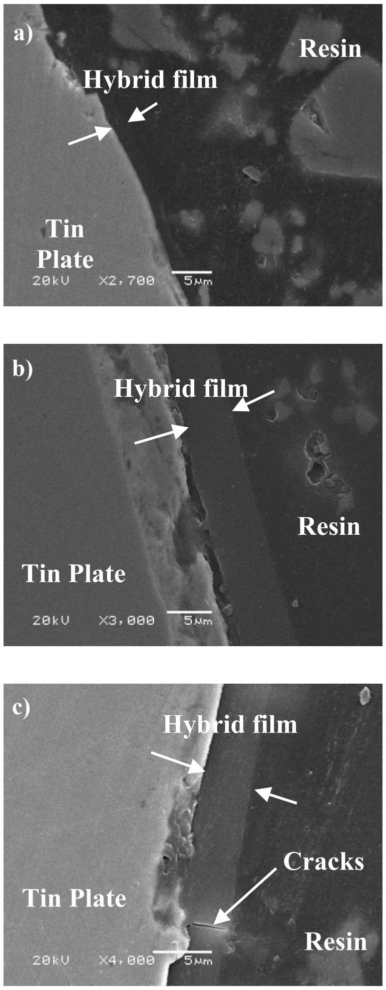


Figure 3. Cross section micrographs obtained by SEM: (a) T1N3, (b) T2N3 and (c) T3N3.
Source: The authors.

Table 2. Thickness of siloxane-PMMA hybrid films.

Samples	Thickness (µm)	Standard deviation (µm)
T1N3	1.36	0.39
T2N3	5.71	0.22
T3N3	4.07	0.27

Source: The authors.

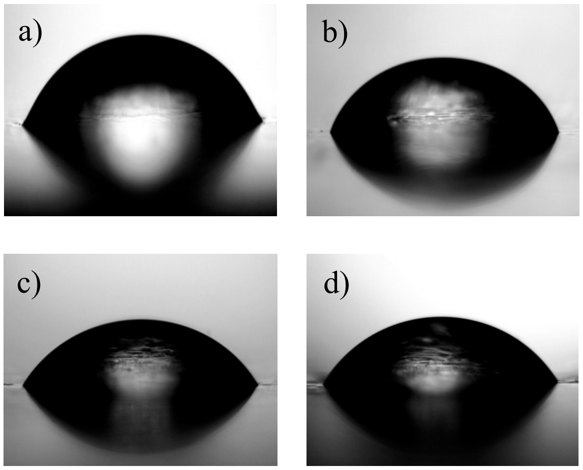


Figure 4. Images obtained for the contact angle determination by the sessile drop method: (a) tin plate, (b) T1N3, (c) T2N3 and (d) T3N3.
Source: The authors.

Table 3. Contact angle values obtained by the sessile drop method.

Samples	Contact Angle	Standard deviation
Tin plate	73°	1.9
T1N3	69°	0.5
T2N3	65°	0.6
T3N3	58°	0.4

Source: The authors.

The results of the contact angle area showed in Figure 4 and Table 3. The value of the contact angle obtained for tin plate (Figure 4-a and Table 3) is associated with the fact that this behavior is probably due to the presence of tin oxides (SnOx), as SnO, SnO_2 and its hydrated forms, which confer a complete or partial coverage of the surface, increasing substrate hydrophobicity. The hybrid film T1N3 showed the highest contact angle value and, consequently, lower wettability. This behavior is related to the formation of more siloxane groups in the sample with TEOS, forming a more compact network preventing the absorption of water, making the film more hydrophobic. Regular morphology can be observed (Figure 2-b). The sample T3N3 showed the highest wettability (lowest contact angle values), among the samples studied. This behavior can be associated to the hydrophilic behavior resulting from excessive TEOS addition [22] and also to the film.

3.2. Electrochemical characterization

Measurements of open circuit potential (OCP) were made in order to monitor the variation of potential with soaking time in 0.05 M NaCl solution as illustrated in Figure 5. The samples T1N3 and T2N3 showed that these films presented open circuit potential values displaced towards passive potentials related to the tin plate substrate, i.e., the hybrid films obtained promoted the formation of a barrier between the substrate and the medium. This is due to the formation of PMMA chains cross-linked with polysiloxane nanodomains, hindering the passage of the electrolyte through the film towards the substrate (tin plate). Sample T3N3 suffered electrolyte permeation due to the presence of cracks on the film surface, as well as delamination problems; henceforth, the OCP values for this sample were more active than the ones for the tin plate substrate and the other studied systems.

OCP shows stabilization after 1200 seconds of soaking time for all the hybrid films due to surface homogeneity, shown in T1N3 and T2N3 by the regular morphology of the obtained film, as observed in the SEM micrographs (Figure 1-a, Figure 1-b). Meanwhile, for the system T3N3, OCP stabilization can be explained because there was the formation of tin oxides due to the electrolyte permeation provoked by cracks and delamination.

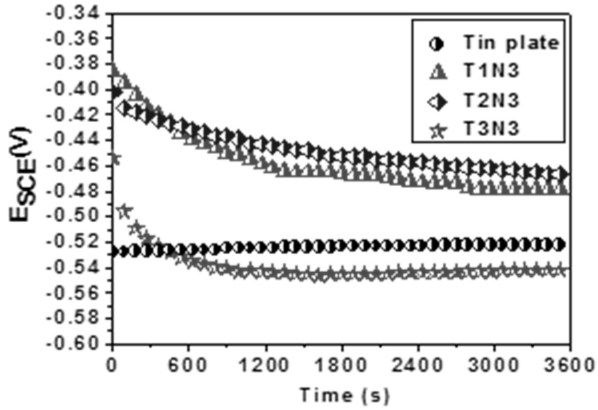


Figure 5. Open circuit potential curves for the films (T1N3, T2N3 and T3N3) and for tin plate without coating.
Source: The authors.

The results (Fig. 6-b and Table 4) showed that the hybrid films siloxane-PMMA with nitric acid and pH=3 (T1N3, T2N3 and T3N3) promoted the increase in polarization resistance (Rp) and the decrease in corrosion current density (icorr) values related to tin plate, evidencing the protective behavior of these films.

All the studied hybrid films displaced the corrosion potential towards the cathodic side, meanwhile they diminished the corrosion current density and increased the polarization resistance, as can be observed in Fig. 6 and Table 4. Compared to tin plate, T1N3 and T2N3 reduced the corrosion current density by one order of magnitude and the polarization resistance for these samples augmented by two orders of magnitude. T3N3 kept the corrosion current density in the same order of magnitude as tin plate but increased the polarization resistance just in one order of magnitude. It is in agreement with that observed in the OCP monitoring results. These phenomena can be explained regarding the amount of TEOS present in the precursor solution of sample T3N3, since the excess of TEOS bring about the formation of a porous ceramic structure, which is brittle. Hence, excess TEOS could promote the formation of cracks that allow the electrolyte to permeate, making the film T3N3 less polarization resistant [23].

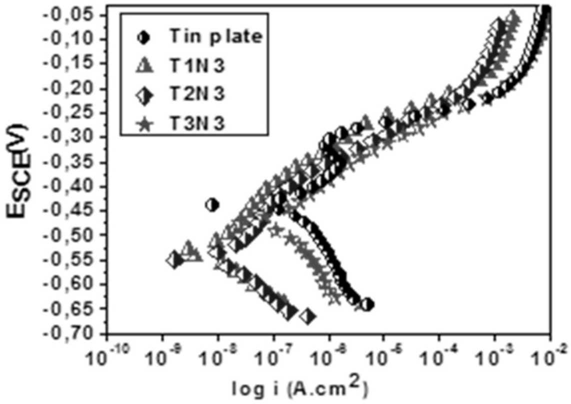


Figure 6. Polarization curves in a 0.05M NaCl solution.
Source: The authors.

Table 4. Obtained data from Tafel extrapolation.

Samples	i_{corr} (A/cm²)	E_{corr}	Rp (Ω.cm²)
Tin plate	4.71×10^{-7}	-439	5.54×10^{4}
T1N3	1.87×10^{-8}	-534	1.40×10^{6}
T2N3	3.25×10^{-8}	-547	8.01×10^{6}
T3N3	2.62×10^{-7}	-472	1.01×10^{5}

Source: The authors.

The anodic branch of the polarization curve is very similar for all the hybrid films meanwhile the tin plate shows a small passivation region caused by tin oxides. For the hybrid films, the anodic reaction is not inhibited by high potential, associated to two factors: lower O_2 diffusion or cathodic area decreasing.

Figure 7 and Figure 8 show electrochemical impedance Bode diagrams for hybrid siloxane-PMMA films (T1N3, T2N3 and T3N3) and for tin plate substrates obtained for 24 and 96 hours, respectively, of immersion in a 0.05 M NaCl solution.

After 24 h of immersion (Figure 7), tin plate presented only one time constant in the medium to low frequency range, which was attributed to a passivating top layer of tin oxides (SnOx), such as SnO, SnO_2 [24]. The hybrid siloxane-PMMA films (T1N3, T2N3 and T3N3) films showed a time constant at a higher frequencies range, less intense than that observed in 24 hours of immersion, and a time constant in the medium to low frequency range, indicating overlapped time constants (Figure 7). The high frequency phenomenon is associated with the barrier properties of the siloxane-PMMA film. On the other hand, the phenomenon observed at the medium to low frequency, indicates an acceleration of the interfacial process associated with the tin oxides on the substrate surface [25]. After 96 h of immersion (Figure 8), tin plate presented two overlapped time constants, indicating the degradation of the tin oxides. At the end of the experiment, red corrosion products were observed on the electrode surface, indicating that during the experiment, iron was dissolved and diffused to the surface forming iron oxides (Figure 9-a).

For the T3N3 film, a time constant observed in high frequency for 24h disappears, possibly related to poor and/or very cracked film formation. Besides, a time constant is observed in the medium to low frequency range, indicating an acceleration of the interfacial process associated with the tin oxides on the substrate surface.

In Figure 8, the samples T1N3 and T2N3 film presents one time constant at high frequency, but less significant than 24 hours of immersion in NaCl 0.05M. This could be explained by the T1N3 and T2N3 film structure where the radical of MMA covalently bonds to the TMSM moieties through polymerization reactions that can only interact by weak Van der Waals forces. Taking into account these structural considerations, a lower thickness of the film is expected, due to the weak bonds (Figure 3 and

Table 2), and consequently not resistant to long periods of immersion in a NaCl 0.05 M solution. In this film, a time constant in the medium to low frequency range was also observed, indicating an acceleration of the interfacial process associated with the tin oxides on the substrate surface.

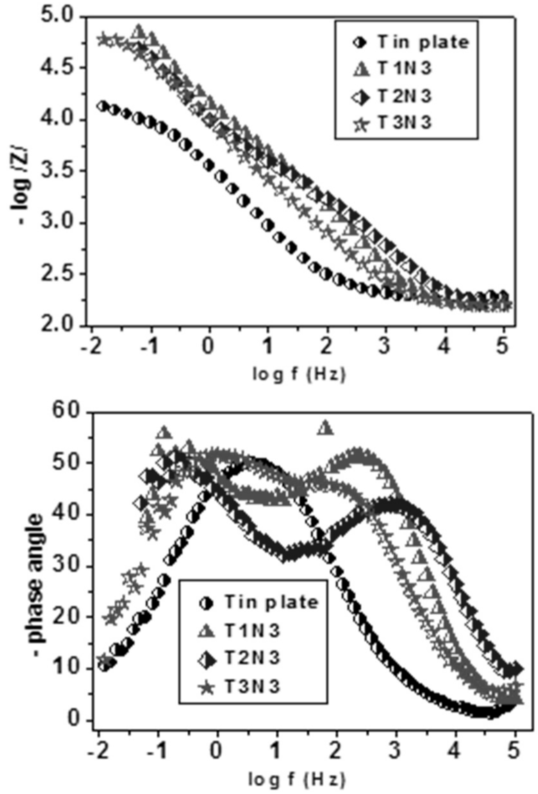
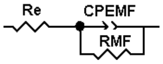
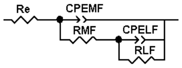


Figure 7. Bode diagrams obtained for the uncoated tin plate and post-treated with siloxane-PMMA hybrid films in a 0.05 M NaCl solution: 24 hours immersion.
Source: The authors.

Table 5.
Electrical elements fitted values for tin plate for 24 and 96 h of immersion in a 0.05M NaCl solution.

Tinplate	24h	96h
Fitted circuit		
Re (Ω.cm^2)	1586	157.9
CPEHF (Fcm^{-2})		
n		
RHF (Ω.cm^2)		
CPEMF (Fcm^{-2})	1.86 x 10^{-6}	2.86 x 10^{-5}
n	0.83	0.78
RMF (Ω.cm^2)	2.85 x 10^5	3.91 x 10^2
CPELF (Fcm^{-2})		3.02 x 10^{-4}
n		0.49
RLF(Ω.cm^2)		7.28 x 10^3

Source: The authors.

Electrical circuit models were used to fit impedance curves. Table 5, Table 6, Table 7 and Table 8 show electrical elements values obtained by fitting for coated and uncoated tin plate at 24 and 96 h of immersion in 0.05 M NaCl solution. In the circuits, capacitances were substituted by constant phase elements (CPE) in order to take into account the non-ideality of the tin plate and hybrid films. A value of n=1 corresponds to smooth surface, therefore CPE should be substituted by an ideal capacitor C. n=0.5 suggests a response of diffusion or porous material, and 0.5<n<1 was associated to heterogeneous, rough or non-homogeneous current distribution [26,27]. On the other hand, Re is the electrolyte resistance, RMF and CPEMF represent a medium frequency range which was attributed to the tin oxides (SnOx), passivating top layer [24]. RHF and CPEHF represent a higher frequency range, associated to the siloxane-PMMA film. RLF and CPELF represent a low frequency range phenomenon, associated to the degradation of the tin oxides.

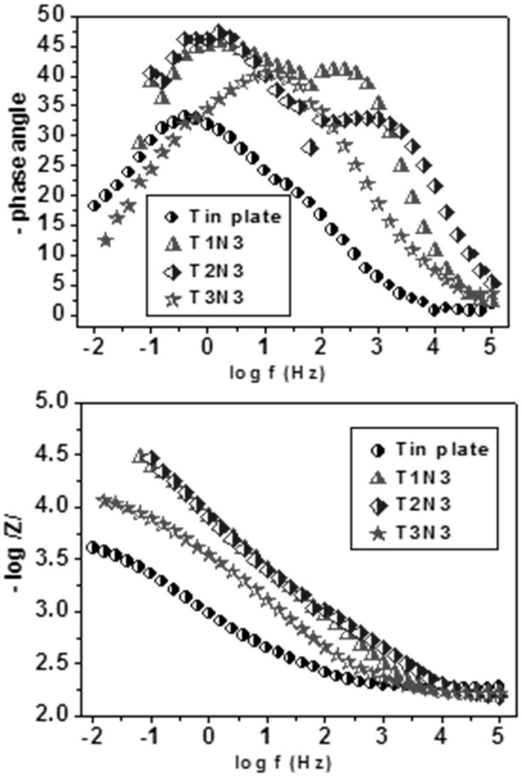
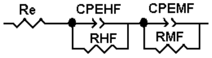
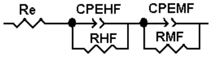


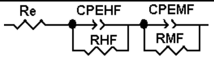
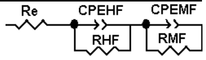
Figure 8. Bode diagrams obtained for the uncoated tin plate and post-treated with siloxane-PMMA hybrid films in a 0.05 M NaCl solution: 96 hours immersion.
Source: author

Table 6.
Electrical elements fitted values for T1N3 for 24 and 96 h of immersion in a 0.05M NaCl solution.

T1N3	24h	96h
Fitted circuit		
Re (Ω.cm^2)	158.2	161.2
CPEHF (Fcm^{-2})	4.12 x 10^{-6}	5.20 x 10^{-6}
n	0.77	0.78
RHF (Ω.cm^2)	4392	1280
CPEMF (Fcm^{-2})	2.16 x 10^{-5}	3.36 x 10^{-5}
n	0. 59	0.59
RMF (Ω.cm^2)	6.47 x 10^9	5.73 x 10^4

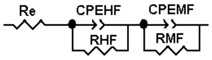
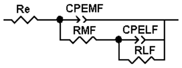
Source: The authors.

Table 7. Electrical elements fitted values for T2N3 for 24 and 96 h of immersion in a 0.05M NaCl solution.

T2N3	24h	96h
Fitted circuit		
Re (Ω.cm^2)	141.0	139.2
CPEHF (Fcm^{-2})	5.47 x 10^{-6}	4.59 x 10^{-5}
n	0.71	0.68
RHF (Ω.cm^2)	1445	531.7
CPEMF(Fcm^{-2})	2.66 x 10^{-5}	4.59 x 10^{-5}
n	0.62	0.57
RMF (Ω.cm^2)	1.98 x 10^4	3.91 x 10^2

Source: The authors.

Table 8.
Electrical elements fitted values for T3N3 for 24 and 96 h of immersion in a 0.05M NaCl solution.

T3N3	24h	96h
Fitted circuit		
Re (Ω.cm^2)	149.4	152.0
CPEHF (Fcm^{-2})	3.38 x 10-5	
n	0.73	
RHF (Ω.cm^2)	590.2	
CPEMF (Fcm^{-2})	3.22 x 10-5	6.95 x 10-5
n	0.64	0.61
RMF (Ω.cm^2)	1.18 x 105	1.21 x 103
CPELF (Fcm^{-2})		5.81 x 10-4
n		0.44
RLF (Ω.cm^2)		7.45 x 103

Source: The authors.

Figure 9 shows the images obtained after 96 hours of EIS in 0.05 M NaCl. At the end of the experiment, red corrosion products were observed on the electrode surface, indicating the formation of iron oxides. The hybrid films obtained with nitric acid (pH=3) and excess TEOS addition (T3N3) showed more red corrosion products on the electrode surface, indicating the formation of iron oxides (Figure 9-d), and hybrid films obtained with nitric acid (pH=3) and with

addition of TEOS (level 2, increased concentration of TEOS in the level 1) T2N3 showed corrosion products from darkening indicating degradation of the tin oxides (Figure 9-c) when compared to the hybrid films obtained with nitric acid (pH=3) with the lowest amount of TEOS (T1N3) (Figure 9-b), as was expected by the results of the EIS bode diagrams (Figure 7 and Figure 8).

4. Conclusions

From the obtained results, it was verified that hybrid siloxane-PMMA films (T1N3 and T2N3) promoted the polarization resistance increase and the corrosion current decrease compared to the uncoated tin plate substrate and T3N3, evidencing the protective effect of these coatings in saline solutions. A shift in open circuit potential to less active potentials was observed after hybrid films application.

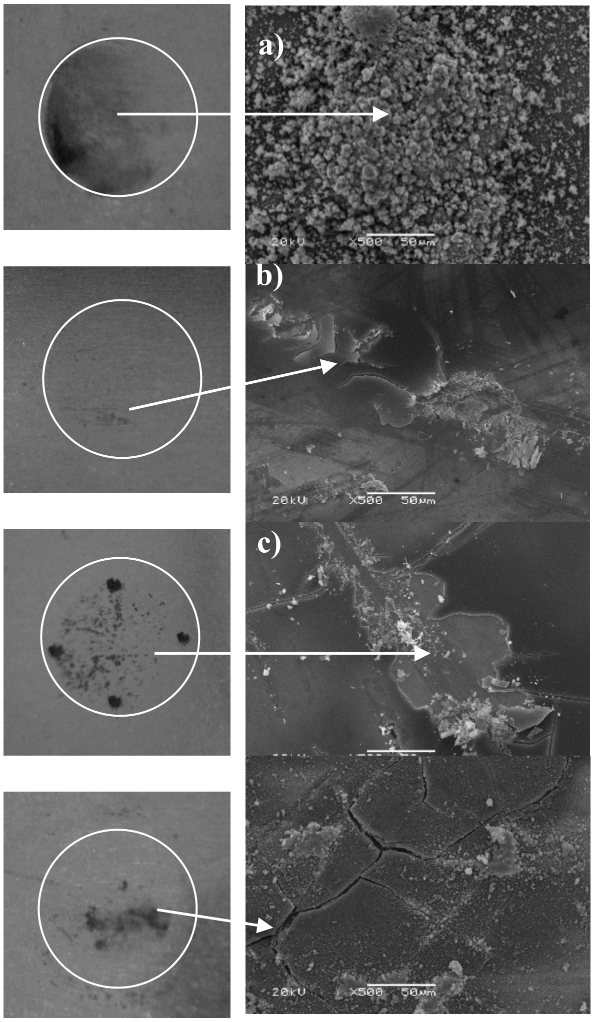


Figure 9. Micrographs obtained after 96 hours of EIS in 0.05 M NaCl: (a) tin plate, (b) T1N3, (c) T2N3 and (d) T3N3.
Source: The authors.

Moreover, the systems showed the best performance in the electrochemical tests, evidencing greater resistance to corrosion even after 96 hours of immersion in saline solution. Furthermore, this film presented a hydrophobic behavior, evidenced by higher contact angle values and, consequently, lower wettability compared to the T3N3 film. It also showed a more regular coverage and lower roughness.

The hybrid film siloxane-PMMA obtained with higher addition of TEOS (T3N3) showed greater thickness, however, due to intense densification of the film promoted by the addition of TEOS, there was the formation of cracks, thereby compromising the corrosion resistance. This is linked to the fact that TEOS addition leads to a permeable structure, which is brittle and further contributes to irregular coverage of the surface and to the poor corrosion protection results as shown in the electrochemical characterization.

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References

[1] Hu, H., Li, N., Cheng, J. and Chen, L., Corrosion behavior of chromium-free dacromet coating in seawater, Journal of Alloys and Compounds, 472, pp. 219-224, 2009. http://dx.doi.org/10.1016/j.jallcom.2008.04.029

[2] Trabelsi, W., Triki, E., Dhouibi, L., Ferreira, M.G.S. and Montemor, M.F., An electrochemical and analytical assessment on the early corrosion behavior of galvanized steel pretreated with aminosilanes. Surface & Coatings Technology, 2004.

[3] Sarmento, V.H.V., Dahmouche, K., Pulcinelli, S H., Santilli, C.V. and Craievichi, A.F., Small- angle X-ray and nuclear magnetic resonance study of siloxane-PMMA hybrids prepared by the sol gel process, Journal of Applied Crystallography, 36, pp. 473-477, 2003. http://dx.doi.org/10.1107/S0021889803000384

[4] Bernardo, P.E.M., Camargo, C.D., Costa, N.G., Avaliação do processo de corrosão em folhas de flandres com e sem revestimento orgânico interno, utilizadas em conservas de pêssego, 6° COTEQ – Conferência sobre Tecnologia de Equipamentos, Brasil, Bahia, 2002.

[5] Dóhler, H., Ferenz, M., Herweth, S., Utilização de silanos epóxi-funcionais como aditivos de aderência para revestimentos de liberação de silicone – Patente PI0603786-0A, 2007.

[6] Cangialosi, D., Mcgrail, P.T., Emmerson, G., Valenza, A., Calderaro, E. and Spadaro, D., Properties and morphology of PMMA/ABN blends obtained via MMA in situ polymerization through γ-rays, Nuclear Instruments & Methods in Physics Research B, 185, pp. 262-266, 2001. http://dx.doi.org/10.1016/S0168-583X(01)00805-9

[7] Shieh, Y.T., Liu, K.H. and Lin, T.L., Effetc of supercritical CO2 on morphology of compatible crystalline/amorphous PEO/PMMA blends, The Journal Supercritical Fluids, 28, pp. 101-112, 2004. http://dx.doi.org/10.1016/S0896-8446(03)00009-3

[8] Langroudi, A.E., Gharazi, S., Rahimi, A. and Ghasemi, D., Synthesis and morphological study on the nanocomposite hydrophilic coatings, Applied Surface Science, 255, pp. 5746-5754, 2009. http://dx.doi.org/10.1016/j.apsusc.2008.12.078

[9] Kozhukharov, S., Kozhukharov, V., Schem, M., Aslan, M., Wittmar, M., Wittmar, A. and Veith, M., Protective ability of hybrid nano-composite coatings with cerium sulphate as inhibitor against corrosion of AA 2024 aluminium alloy, Progress in Organic Coatings, 73, pp. 95-103, 2012. http://dx.doi.org/10.1016/j.porgcoat.2011.09.005

[10] Fedel, M., Druart, M.E., Oliver, M., Poelman, M., Deflorian, F. and Rossi, S., Compatibility between cataphoretic electro-coanting and silane surface layer for the corrosion protection of galvanized steel, Progress in Organic Coatings, 69, pp. 118-125, 2010. http://dx.doi.org/10.1016/j.porgcoat.2010.04.003

[11] Montemor, M.F. and Ferreira, M.G.S., Electrochemical study of modified bis-[triethoxysilylpropyl] tetrasulfide silane films applied on the AZ31 Mg alloy. Electrochimica Acta, 52, pp. 7486-7495, 2007. http://dx.doi.org/10.1016/j.electacta.2006.12.086

[12] Gu, S., Kondo, T. and Konno, M., Preparation of silica–polystyrene core–shell particles up to micron sizes. J. Colloid Interface Sci., 272, pp. 314-320, 2004. http://dx.doi.org/10.1016/j.jcis.2004.01.056

[13] Luna-Xavier, J., Guyot, A. and Bourgeat-Lami, E., Synthesis and characterization of silica/poly (methyl methacrylate) nanocomposite latex particles through emulsion polymerization using a cationic azo initiator. J. Colloid Interface Sci., 250, pp. 82-92, 2002. http://dx.doi.org/10.1006/jcis.2002.8310

[14] Sertchook, H. and Avnir, D., Submicron silica/polystyrene composite particles prepared by a one-step sol–gel process. Chem. Mater., 15, pp. 1690-1694, 2003. http://dx.doi.org/10.1021/cm020980h

[15] Park, J.U., Kim, W.S. and Bae, B.S., Photoinduced low refractive index in a photosensitive organic-inorganic hybrid material, Journal of Materials Chemistry, 13, pp. 738-741, 2003. http://dx.doi.org/10.1039/b211094f

[16] Zhu, A., Shi, Z., Cai, A., Zhao, F. and Liao, T. Synthesis of core-shell PMMA-SiO2 nanoparticles with suspension-dispersion-polymerization in an aqueous system and its effect on mechanical properties of PVC composites, Polymer Testing., 27, pp. 540,547, 2008.

[17] Katsikis, N., Zahradnik, F., Helmschrott, A., Munstedt, H. and Vital, A., Thermal stability of poly(methyl methacrylate)/silica nano- and microcomposites as investigated by dynamic-mechanical experiments, Polym. Degrad. Stab. 92, pp. 1966-1976, 2007. http://dx.doi.org/10.1016/j.polymdegradstab.2007.08.009

[18] Delattre, L., Dupuy, C. and Babonneau, F., Characterization on the hydrolysis and polymerization processes of methacryloxypropyltrimethoxylane, Journal of Sol-gel Science and Thecnology, 2, pp. 185-188, 1994. http://dx.doi.org/10.1007/BF00486238

[19] ATMS - G01 Committee, ASTM G5 - Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements, ASTM International, 4, 2013.

[20] G01 Committee, ASTM G106 - Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements, ASTM International, 2010.

[21] Zhang, X., Wu, Y., He, S. and Yang, D., Structural characterization of sol–gel composites using TEOS/MEMO as precursors, Surf. Coat. Technol., 201, pp. 6051-6058, 2007. http://dx.doi.org/10.1016/j.surfcoat.2006.11.012

[22] Cairú, A. and Mittal, K.L., UV-Resistant and Superhydrophobic Self-Cleaning Surfaces using Sol-gel Process. Ed. Netherlands / Brill; 2009.

[23] Kunst, S.R., Cardoso, H.R.P, Oliveira, C.T., Santana, J.A., Sarmento, V.H.V., Muller, I.L. and Malfatti, C.F., Corrosion resistance of siloxane–poly(methyl methacrylate) hybrid films modified with acetic acid on tin plate substrates: Influence of tetraethoxysilane addition. Applied Surface Science, 298, pp. 1-11, 2014. http://dx.doi.org/10.1016/j.apsusc.2013.09.182

[24] Sakai, R.T., Cruz, F.M.D.L., Melo, H.G., Benedetti, A.V., Santilli, C.V. and Suegama, P.H., Electrochemical study of TEOS, TEOS/MPTS, MPTS/MMA and TEOS/MPTS/MMA films on tin coated steel in 3.5% NaCl solution, Prog. Org. Coatings, 74, pp. 288-301, 2012. http://dx.doi.org/10.1016/j.porgcoat.2012.01.001

[25] Suegama, P.H., Sarmento, V.H.V., Montemor, M.F., Benedetti, A.V., Melo, H.G., Aoki, I.V. and et al., Effect of cerium (IV) ions on the anticorrosion properties of siloxane-poly(methyl methacrylate) based film applied on tin coated steel, Electrochimica Acta, 55, pp. 5100-5109, 2010. http://dx.doi.org/10.1016/j.electacta.2010.04.002

[26] Conde, A. and Damborenea, J., Electrochemical impedance spectroscopy for studying the degradation of enamel coatings, Corros. Sci., 44, pp. 1555-1567, 2002. http://dx.doi.org/10.1016/S0010-938X(01)00149-4

[27] Morales, U.P., Camargo, A.M. and Flóres, J.J.O., Electrochemical Impedance – Interpretation of Typical Diagrams with Equivalent Circuits. DYNA, 77, pp. 69-75, 2010.

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