



Influence of the sol pH in a siloxane-PMMA environmentally friendly coating

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Abstract

Environmentally friendly pre-treatments with a siloxane base - PMMA have shown promising results when combined with the new ink technology with curing by ultraviolet (UV) radiation. Tinplate sheets were coated with a hybrid film obtained from a sol with alkoxides precursors consisting of 3-(trimethoxysilylpropyl) methacrylate and tetraethoxysilane and adding an organic phase composed of poly (methyl methacrylate). The hydrolysis reactions were catalyzed with a nitric acid solution (pH=1 and pH=3). The hybrid films were obtained by a dip-coating process and were coated with red-colored paint UV curing, and characterized for their electrochemical and mechanical behavior. The results showed that a more acidic pH (pH=1) promotes the formation of a hybrid film with better protective properties, presented a better electrochemical performance and higher values of layer thickness. However, the hybrid film was obtained with pH=3 presented best perform with applied to the UV ink, owing to the better anchorage and adhesion.

Keywords: Tinplate. Hybrid film. Silane. pH. UV coating.

Theme Area: clean technologies.

1 Introduction

Many authors aimed their researches on pre greener alternative treatments with free from chromium salts and phosphate-based coatings [FANG et al., 2009]. Among these, we highlight the use of hybrid films formed by the reaction of hydrolysis and condensation of silane pathways. Although it has been demonstrated that the siloxane hybrid films are relatively efficient for the protection of metallic substrates against corrosion, this efficiency depends on many parameters such as pH, concentration changes in the silane solution, solution contamination due to previous steps, as cleaning, for instance [XIAN et al., 2013]. Among these parameters, there is an increased relevance for the study of the influence of pH on the stability of the silane in aqueous solution, and, ultimately, the life of the hydrolysis solution. It is also known that this parameter influences the behavior of silanes during the hydrolysis and condensation reactions, because both reactions are catalyzed by acids or bases [CABRAL et al., 2006; SUEGAMA et al., 2010]. The hydrolysis and condensation reactions in the aqueous phase of the molecules of silanols occur simultaneously in the hydrolysis solution. However, the rate of hydrolysis of most silanes in slightly acidic aqueous solutions is much faster than the rate of condensation.

Besides the significant improvement in corrosion protection of the substrate to which they are applied, these films also confer adhesive properties to organic coatings, providing an excellent anchorage for difficult metal adhesion, such as tin [ÁLVAREZ et al., 2014]. Therefore, the siloxane-based pre-treatments – PMMA have been showing promising results when combined with new ink technology with curing by ultraviolet (UV) radiation. On the one hand, it is known that the UV curing process has many advantages, such as the excellent



physical and chemical properties the film presents, its ease of automation, and the fact that it has an environmentally friendly process. In addition, since the volatile product is part of the reaction, becoming an integral part of the coating, it presents an evaporative loss lower than 5% [FANG et al, 2009]. On the other hand, one of the main problems of the UV curing process is the fact that most of the radiation curable coatings does not present good adhesion when applied directly on metal surfaces. This deficiency is mainly related to poor adherence and shrinkage of the film after curing [CALDERÓN et al., 2007]. That is because inks have been used only because they offer protection as a physical barrier. Thus, due to the difference in the expansion coefficients, the stress and deformation of surfaces, or even the lack of adhesion to the substrate, the coating may be damaged, allowing corrosive agents to permeate the metal substrate [GARCÍA-HERNANDEZ et al., 2009].

In this context, the objective of this work is to develop and characterize and evaluate the performance of corrosion in hybrid films obtained from sol alkoxides precursors consisting of: 3-(trimethoxysilylpropyl) methacrylate (TMSM), tetraethoxysilane (TEOS) with the addition of poly (methyl methacrylate) PMMA. In two of the hydrolysis solutions (1 and 3) varying pH levels were applied. Finally, we aimed to evaluate the performance of corrosion and adhesion of a UV curing ink applied on these hybrid films.

2 Materiais e métodos

Tinplate (samples supplied by CSN) was used as substrates. Two types of silanes were used in this study: (trimethoxysilylpropyl) methacrylate (TMSM) - ($C_{10}H_{20}SiO_5$), > 98% purity, and tetraethoxysilane (TEOS) - ($C_8H_{20}SiO_4$), with a purity of >99.9%, both from Sigma Aldrich. Methyl methacrylate (MMA, Aldrich, 99% purity) – stored in a freezer prior to use, was distilled to remove the polymerization inhibitor (hydroquinone) and the impurities. Benzoyl peroxide, BPO (Reagen), was recrystallized from ethanol.

Tinplates were washed with acetone and dried with hot air. Subsequently, they were degreased with a neutral detergent (pH=7) at 70°C, by immersion, for 10 minutes. They were then rinsed with deionized water, dried once again, washed with acetone, and finally dried with hot air.

The sol-gel method was employed in the preparation of hybrid organic-inorganic materials. In the preparation of the inorganic phase, a synthesis of the precursors and the TMSM TEOS was made. They were combined at 60°C for 1 hour; the hydrolysis was done in an acid medium at two levels by varying the pH value (pH=1 and pH=3), using nitric acid as catalyst and ethanol as solvents, and water. The MMA was homogenized at room temperature, with benzoyl peroxide (BPO) as the thermal initiator. Finally, both of the solutions (organic and inorganic) were combined and stirred for 5 minutes at 45°C to form a transparent sol. The films were obtained by dip-coating process, with a removal rate of 14 cm.min⁻¹. Subsequently, the coated substrates were heat treated (cured) at about 160°C for 3 hours under a heating rate of 5 °C.min⁻¹.

Some of the hybrid films were then coated with a UV curing red paint. The fast peak of the curing equipment at a gallium pressure was doped with a UV mercury lamp using a medium dose of 265 mJ.cm⁻², 395 mW.cm⁻² intensity and a belt speed of 18.5 m.min⁻¹. A UV coating, using the same parameters mentioned above, was also applied on tinplate sheets without pretreatment, for the sake of comparison. Table 1 displays the description of samples.

Table 1 – Description of the samples.

Sample	Description
F1	Uncoated tinplate.
F1N1	Tinplate, coated with a hybrid film acidified with nitric acid (pH = 1)



F1N3	Tinplate, coated with a hybrid film acidified with nitric acid (pH = 3)
F1 _{UV}	Uncoated tinplate, with application of UV paint
F1N1 _{UV}	Tinplate, coated with hybrid film acidified with nitric acid (pH = 1) and with application of UV paint.
F1N3 _{UV}	Tinplate, coated with hybrid film acidified with nitric acid (pH = 3) and with application of UV paint.

Morphological characterization was performed by scanning electron microscopy (SEM) with a JEOL-JSM with an acceleration voltage of 20 kV. The samples were observed from the top view and in a cross-sectional view to determine the layer thickness.

The corrosion performance of the coatings was evaluated by open circuit potential (OCP) monitoring, polarization curves and electrochemical impedance spectroscopy (EIS) measurements in a 0.05 M NaCl solution. This concentration is sufficiently high to activate corrosion in a relatively short exposure time but is low enough to enable the effects of plasticizer to be determined. A three-electrode cell was used to perform the analyses, with a platinum wire as a counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. The area of the working electrode was 0.626 cm². The polarization curves were collected at a scan rate of 1 mVs⁻¹ in a potential interval between 200 mV (below OCP) and 400 mV (above OCP).

For the EIS measurements, the systems were previously monitored for 96 hours. The amplitude of the EIS perturbation signal was a sinusoidal 10 mV (rms) signal, and the frequency range studied was from 100 kHz to 10 mHz using a Solartron 1255 frequency response analyzer, and a Omnimetra Mod. PG-05 potentiostat.

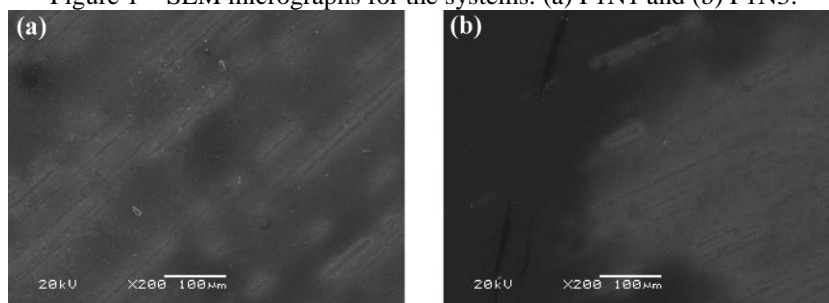
The flexibility test was performed by folding the specimens over a tapered mandrel from TKB Erichsen Instruments. This test is based on the Brazilian Norm NBR 10545 [13]. The crosshatch adhesion test and the tape pull test were performed following ASTM D-3359 [14].

3 Results

Hybrid films.

Figures 1-a and 1-b show the top view SEM micrographs of the samples F1N1 (pH=1) and F1N3 (pH=3), respectively. The morphology of the samples shows a homogeneous film without cracks, and only small discontinuities were observed in both samples.

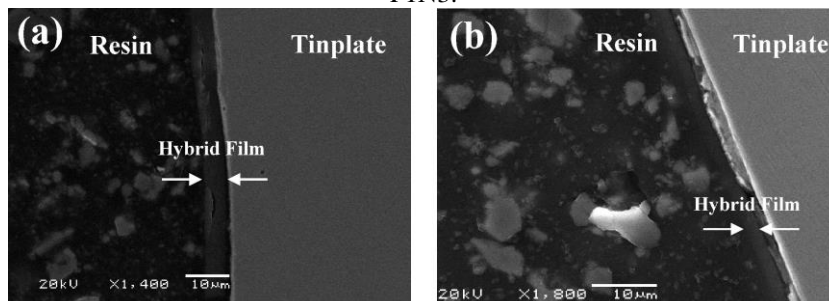
Figure 1 – SEM micrographs for the systems: (a) F1N1 and (b) F1N3.



The layer thickness of the films was determined by analysis of the cross section images obtained by SEM (Figure 2). The F1N1 presented a higher layer thickness ($6 \mu\text{m} \pm 0.45$) than the hybrid film F1N3 ($2.30 \mu\text{m} \pm 0.29$), which was obtained in a less acid means (pH = 3).



Figure 2 – Cross-sectional SEM micrographs to determine the layer thickness for the samples: (a) F1N1 and (b) F1N3.



Open circuit potential measurements were performed to monitor the variation of potential with time of immersion (Figure 3a). From the extrapolation of the Tafel straight line, applied to the polarization curves shown in Figure 3b, the corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and the polarization resistance (R_p) for the studied hybrid films was determined (Table 2).

Figure 3. Open circuit potential (a) and polarization curves (b) obtained for all the studied samples.

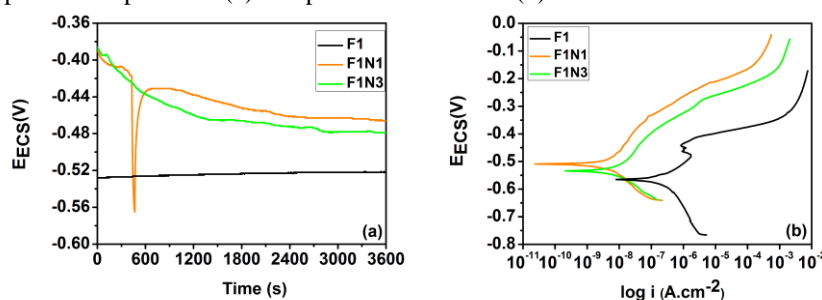


Table 2 – Extrapolation of the Tafel straight line.

Samples	i_{corr} (A.cm ⁻²)	E_{corr} (mV)	R_p (Ω)
F1	$4,71 \times 10^{-7}$	-568	$5,54 \times 10^4$
F1N1	$2,96 \times 10^{-8}$	-502	$1,13 \times 10^6$
F1N3	$1,41 \times 10^{-7}$	-539	$1,85 \times 10^5$

Figure 4 shows the Nyquist for the F1, F1N1 and F1N3 plate samples immersed in a NaCl 0.05 M solution. It is observed that the F1N1 hybrid film showed higher resistance values for all analyzed immersion times (up to 96 hours of immersion).

From the Bode diagram, for 24 h of immersion (Figure 5a), a high-frequency phenomenon was found only for the F1N1 sample, often associated with an efficient barrier effect of the siloxane-PMMA hybrid films. For the F1N3 sample, only one medium frequency phenomenon was observed, which is often associated to the permeability of the electrolyte through the film. For the uncoated tinplate, it was observed after 24 hours of immersion (Figure 5a) only one time constant, associated to the permeability of the electrolyte through the tin oxides on the metallic surface. At 96 hours of immersion (Figure 5b), a second time constant appears for the substrate, in a low frequency, which is probably associated to the corrosion products.



Figure 4 - Nyquist diagrams obtained for the coated samples and for uncoated tinplate in 0.05 M NaCl: (a) 24 hours and (b) 96 hours.

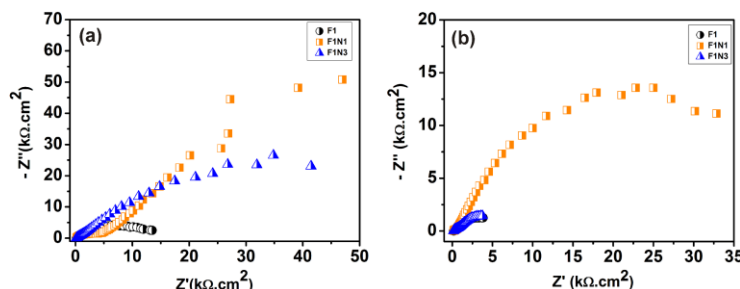
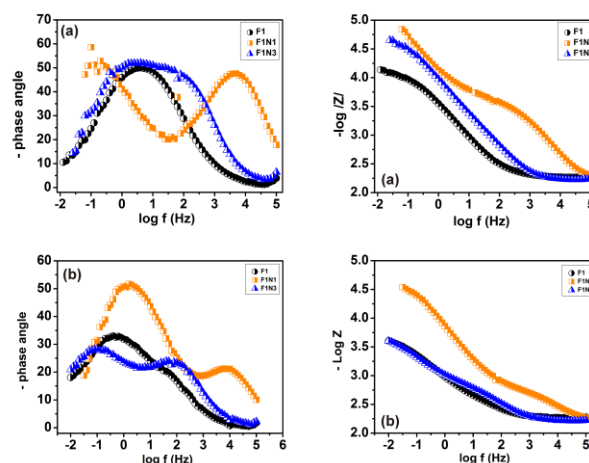


Figure 5 - Bode diagrams obtained for the coated samples and for uncoated tinplate in 0.05 M NaCl: (a) 24 hours and (b) 96 hours.



Sample with UV paint

Figures 6 and 7 show the Nyquist and Bode diagrams, respectively, for the F1UV, F1N1UV and F1N3UV samples immersed in a NaCl 0.05 M solution. The resistive behavior of the F1N1UV sample remained constant and superior, if compared to the other samples throughout the course of the test (Figure 6-a). It is observed also the large reduction of the polarization resistance values between the 24 to 192 hour range, these being approximately 20 times lower than the values obtained in the initial test conditions.

Similarly, the analysis of the Bode test, the F1N1UV system showed the highest values of impedance module during 360 hours. However, when the phase angle data is compared, there is an inversion of this behavior among samples. At low frequencies, the F1N3UV sample presented higher values. The presence of lower stable phase angle values at low and medium frequencies (-2 to 3 Hz) can also be observed. This behavior was more pronounced in the first 24 hours for the F1N1UV sample. Later, in 192 hours, this pattern was observed for the F1N1UV and F1N3UV samples, and, finally, after after 360 hours for all of the systems.



Figure 6 - Nyquist diagrams obtained for the samples coated with hybrids films and painted and for painted without pre-treatment: (a) 24, (b) 192 and (c) 360 hours.

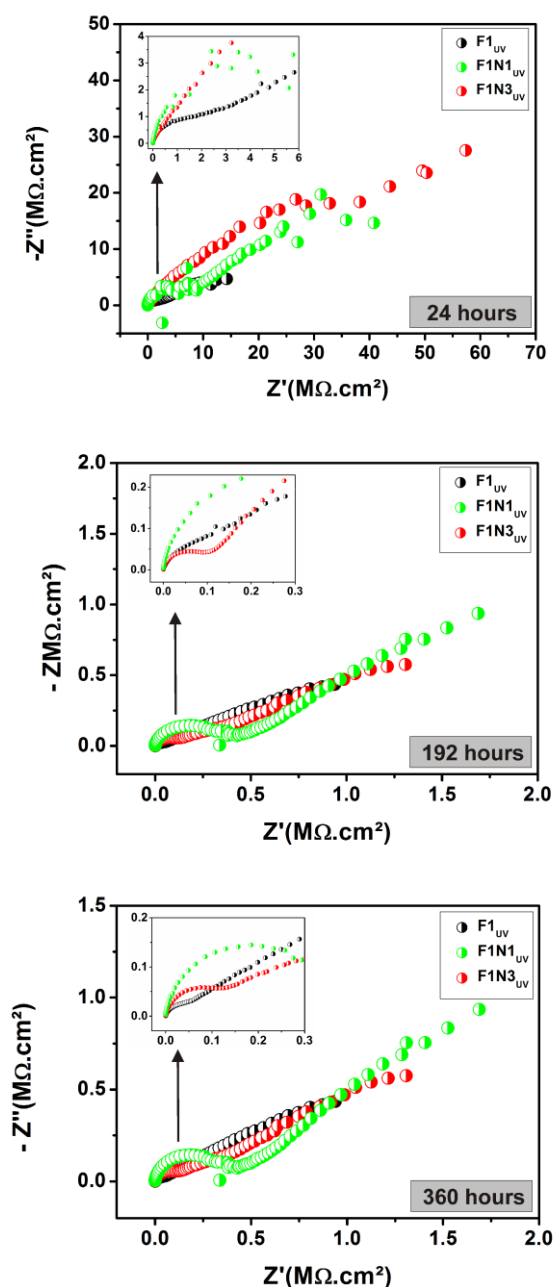
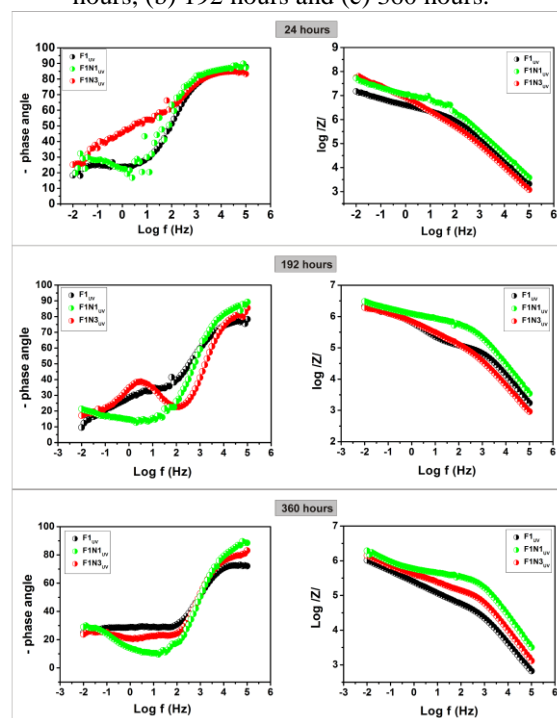


Figure 7 - Bode diagrams obtained for the samples coated with hybrid films and painted, and for the samples painted without pre-treatment: (a) 24 hours, (b) 192 hours and (c) 360 hours.



4 Discussion

The formation of films with great morphological properties demonstrates the excellent interaction between the organic and inorganic phases and homogeneity of siloxane-PMMA hybrid films. Besides, properties such as flexibility and adhesion of the film were achieved



because the correct proportion of PMMA was applied to the film, thus avoiding the formation of cracks and lack of adherence.

A decrease in the value of the layer thickness for the sample with less acidic pH was observed. Results presented in the literature show that the sol viscosity increases with the decrease of the pH [CERTHOUX et al., 2013]. A low pH value (pH=1) favored the hydrolysis of silicon alcoxides (TMSM and TEOS) contributing to formation of near linear siloxane clusters that influenced the sol viscosity, enhancing the film thickness, and the barrier layer formation, thus improving the anticorrosive performance.

The silylation process can be described as a three-step reaction model:

- (1) Si-OR groups turn into Si-OH through a hydrolysis reaction;
- (2) Si-OH groups turn into oligomeric siloxane containing some unreacted Si-OH by a condensation reaction;
- (3) Si-OH groups in the siloxane form hydrogen bonds with the hydroxyl groups on the tinplate foil surface. Then, Si-OH groups form covalent bonds with the tinplate foil through condensation during the heating process [XIA et al., 2013].

For samples without application of UV paint, the EIS results indicate that the low pH contributed for the barrier layer formation, thus promoting the increase of film thickness, making the film denser and improving anticorrosion performance. The poorly performing anticorrosion of the sample with pH less acidic may be associated to the fact that the film presents a lower hydrolysis rate of the inferior silane molecules, decreasing the number of silanol groups, and thus resulting in a lower formation of siloxane groups. This hinders the formation of the barrier layer, as evidenced with the resulting low layer thickness for this sample.

For samples with application of UV paint, the EIS results indicate that the low frequencies can refer to a process of occurrence of corrosion of the metal substrate without the intervention of a minimal coat of paint, for it does not provide a satisfactory protective performance [OLIVEIRA, 2003]. Regarding the center frequencies, they could be due to the appearance of small bubbles in the applied ink layer. In any case, this phenomenon was not observed in the tested samples.

According to this result, the F1N1UV it is possible to notice that this sample showed a better barrier layer, which is corroborated by the higher film thickness, hence improving its anticorrosive performance. Nevertheless, the UV coating does not perform well on this film because the lower solution pH induces an increase in the cross-linking reactions, reducing its reactivity. This loss of reactivity is caused by the conversion of the silanol groups into siloxanes. As a result, the film becomes dense, rigid and the reactions conducting to adhesion of the paint become more difficult.

According to mechanical characterization results, for the F1N1UV sample it is possible to notice that this sample showed a better barrier layer, which is corroborated by the higher film thickness, hence improving its anticorrosive performance. Nevertheless, the UV coating does not perform well on this film because the lower solution pH induces an increase in the cross-linking reactions, reducing its reactivity. This loss of reactivity is caused by the conversion of the silanol groups into siloxanes. This film becomes dense, rigid and the reactions conducting to adhesion of the paint become more difficult. The sample with pH less acidic showed the lowest coefficient of friction and the greatest distance of accommodation, thus characterized by having the best performance wear. This result confirms the flexibility and adhesion by this system in the mechanical tests already discussed earlier.



5 Conclusions

Hybrid siloxane-PMMA films obtained using a more acidic environment (pH=1) showed a better electrochemical performance and higher layer thickness values. This behavior can be attributed to the fact that the low pH solution favored the hydrolysis of silicon alcoxides (TMSM and TEOS), contributing to the formation of near linear siloxane clusters that exert influence on the viscosity of hybrid films, thus increasing film thickness, forming the barrier layer and consequently improving the anti-corrosion performance. However, the F1N3UV sample, obtained at pH=3, had a better performance as a pretreatment for subsequent application of the UV-curing coating, contributing to the adhesion of this paint.

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