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SCIENTIFIC PAPER

UDC 669.715:678:544:543.42

<https://doi.org/10.2298/CICEQ150725013K>

EFFECT OF DIISODECYL ADIPATE CONCENTRATION IN HYBRID FILMS APPLIED TO TINPLATE

Article Highlights

- Tinplate protection from corrosion
- Flexible hybrid film obtained by sol-gel process
- Electrochemical impedance spectroscopy tests

Abstract

Siloxane hybrid films are fragile and have low mechanical strength due to their vitreous material properties. Hence, a new formulation incorporating a plasticizer agent was developed in order to increase the layer thickness of a uniform and homogeneous hybrid film on tinplate, and to provide flexibility to the polymeric matrix. Tinplate sheets were coated with a hybrid film obtained from a sol-gel process, constituted by the addition of the following alkoxide precursors: 3-(trimethoxysilyl) propyl methacrylate and tetraethoxysilane with 0.01 mol L⁻¹ cerium nitrate addition. The influence of the diisodecyl adipate plasticizer concentration was evaluated. The films were characterized by scanning electron microscopy, profilometry, open circuit potential monitoring, polarization curves and electrochemical impedance spectroscopy. The results showed that all films with diisodecyl adipate had higher electrochemical performance compared to uncoated tinplate. However, the film with the 2% plasticizer concentrations had the best performance in the electrochemical tests, although it had thinner layer.

Keywords: hybrid film, diisodecyl adipate, tinplate, electrochemical behaviour.

The sol-gel process is a widely researched and used technology [1-5], as a result of the obtained surface protection properties, the simplicity of the formulation process and its economic viability. Among its advantages, the following can be mentioned: the stoichiometry is easy to control and adjust [6]; it is possible to tailor a film with high purity and with a uniform distribution of the components [7]; the process can be carried out under normal pressure and low temperatures [8-12]. Furthermore, the sol-gel process has been used for decades to obtain a high number of hybrid materials, using inorganic and polymeric precursors [13,14].

The sol-gel process consists of the hydrolysis and condensation of alkoxide precursors with metal-oxane, in order to obtain a three-dimensional siloxane network. After deposition of the film on the substrate by means of appropriate techniques, the film is exposed to air at the beginning of the condensation reaction. After a few minutes of drying, a network (gel) is formed on the substrate [15,16]. The formed network is a hybrid (organic and inorganic) [16]. Water molecules are eliminated through sintering (densification) at an appropriate temperature, and a compact hybrid layer is formed. Then, the film is submitted to a final thermal treatment for structure control [17].

Hybrid films are used to coat a variety of metallic substrates to protect them from corrosion [18,19]. Amongst these, tinplate can be mentioned. Tinplates are used in food and non-food packaging applications [20]. For good quality, the presence of tin oxides on the surface and the condition of the passivation layer are very relevant. The presence of such oxides can

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Paper received: 25 July, 2015
Paper revised: 6 November, 2015
Paper accepted: 11 March, 2016

alter the sheet appearance, weldability and capability of being coated with organic films [21]. Currently, many surface treatments for packaging are based on chromates, as they offer excellent corrosion resistance, but their application process is highly toxic. Thus, non-toxic pre-treatment alternatives have been developed recently to replace the chromating process [22,23]. Hybrid films obtained by the sol-gel process are one of those alternatives and the industrialization of the sol-gel process involves work with real substrates [16,24-26].

Research has been performed on the tinplate coating with hybrid films. Kunst *et al.* [27] studied the coating the tinplate with mono and bilayer of hybrid films modified with polyethylene glycol (PEG). These hybrid films were obtained from precursors 3-(trimethoxysilyl)propylmethacrylate (TMSM) and tetraethoxysilane (TEOS) with the addition of cerium nitrate in a concentration of 0.01 M. The hybrid films were applied in single and double layers and cured at different temperatures (60 and 90 °C). The hybrid film with monolayer and cured at 90 °C showed a more compact, uniform, less porous layer and better electrochemical impedance results.

Kunst *et al.* [28] studied the effect of the concentration of tetraethoxysilane (TEOS) on the protective properties of the film on tinplate substrate. The tinplate was coated with a hybrid film obtained from a sol-gel method constituted of the alkoxide precursors 3-(trimethoxysilyl)propylmethacrylate (TMSM) and poly(methyl methacrylate) (PMMA) and different concentrations of tetraethoxysilane (TEOS). The hydrolysis of these films was performed at a pH value of 3 using acetic acid as a catalyst. All the studied films have shown good performance as to corrosion resistance on tinplate, but the film with ratio TEOS:MPTS of 1 showed the best electrochemical results.

Kunst *et al.* [29] studied protective coatings as hybrid films composed by different acids are studied to improve the barrier effect against corrosion. The hybrid films deposited on a tinplate from a sol made up of the alkoxide precursors 3-(trimethoxysilyl)propylmethacrylate (TMSM), tetraethoxysilane (TEOS) and poly(methylmethacrylate) (PMMA) with benzoyl peroxide (BPO). The hybrid sols were prepared by mixing water with three different acids: acetic (CH₃COOH), hydrochloric (HCl) and nitric acid (HNO₃). The results demonstrate that the hybrid film obtained by acetic acid addition exhibiting the greatest improvement the protective properties of the tinplate.

Malfatti *et al.* [30] showed that the addition of Ce³⁺ in a hybrid films confers additional active corrosion protection through a self-healing behavior that

can be verified by the reduction in corrosion rate compared to hybrid films without Ce³⁺ addition. Thus, considering the industrial potential for application of the coating, it is expected that the Ce³⁺ should decrease the corrosion process in case of damage to the barrier layer.

In order to improve the barrier effect and coat the tinplate uniformly and homogeneously, it is desirable to obtain coatings with higher layer thickness. For this purpose, there are two possible approaches: one is to increase the number of layers up to a limit number to avoid delamination [31]. An alternative approach is to increase the sol viscosity; this parameter can be modified either by varying the temperature to alter the hydrolysis and condensation reaction kinetics during the siloxane film formation, or by introducing a plasticizer agent to modify the intrinsic properties of the gel. The latter was chosen in this study, due to the fact that it is easily adjustable [15].

The purpose of this work was to coat tinplate with hybrid film, obtained from a sol-gel process. This film was constituted by the alkoxide precursors 3-(trimethoxysilyl)propyl methacrylate (TMSM) and tetraethoxysilane (TEOS) and was added different diisodecyl adipate plasticizer concentrations (0.5, 1, 2 and 4%). The films were applied using a by dip-coating process and were cured at 60 °C for 20 min. From this study, an ideal concentration of diisodecyl adipate plasticizer was determined for the training of a hybrid film with protective properties superior to other films studied.

MATERIALS AND METHODS

Surface preparation

Tinplate coupons with dimensions of 20 mm×40 mm were obtained from industrial sheet, rinsed with acetone and dried. The tinplate used in this study has the maximum percentage composition of: 0.06C, 0.2Mn, 0.02P, 0.02S, 0.005N and 0.06Al. The average thickness of the tinplate used was 0.245 mm. The used tinplate had yield strength ranging from 210 to 310 MPa, tensile strength of 290 to 410 MPa, hardness of 51 to 59 HR 30 T D and tin coating of 3.0 to 2.0 g m⁻². The plate samples were degreased with a 10 min immersion in neutral detergent at 70 °C, washed and dried.

Hybrid films elaboration

Hydrolysis reactions were conducted with the silane precursors 3-(trimethoxysilyl)propylmethacrylate (TMSM, C₁₀H₂₀SiO₅) and tetraethoxysilane (TEOS, C₈H₂₀SiO₄), with 0.01 mol L⁻¹ cerium nitrate

addition, and water and ethanol were used as solvents. The TEOS/TMSM/H₂O/EtOH proportions were, respectively, 25/4/16/55 wt.%. A diisodecyl adipate plasticizer was added to the sol formulation in four different concentrations (0.5, 1, 2 and 4 wt.%); a sample without plasticizer addition also was analyzed. The hydrolysis time was of 24 h at 25 °C. A dip-coating process was conducted to coat the substrate with the hydrolyzed hybrid solution, with a removal rate of 10 cm min⁻¹ and a residence time of 5 min. After the dip-coating process, the hybrid film pre-treated substrates were thermally oven-cured at 60±2 °C for 20 min.

Table 1 presents the description of the studied samples, and the entire protocol of the sol preparation and coatings is detailed in the flow chart presented in Figure 1.

Experimental techniques

Morphological characterization was performed using a JEOL 6060 scanning electron microscope (SEM) at an acceleration voltage of 20 kV. The samples were observed from top surface view and in a cross-section to determine the layer thickness. The surface micro-roughness was evaluated in a contact profilometer (PRO500 3D). The wettability of the hybrid films was evaluated by contact angle measurements through the sessile drop method in equipment developed by the Laboratory of Corrosion Research (LAPEC) at UFRGS. The contact angle was determined using image analysis software.

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 mol L⁻¹ NaCl solution. All electrochemical tests were performed in triplicate, in an environment temperature and without aeration. This concentration is sufficiently high to activate corrosion in a relatively short exposure time but is low enough to enable the effects of the plasticizer to be determined. Kozhukharov *et al.* [32] also used 0.05 mol L⁻¹ NaCl to ensure a sufficiently low concentration to allow for the observation of corrosion inhibitor effects. A three-electrode cell was used to perform the evaluations, with a platinum wire as the 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 mV s⁻¹ and potential intervals between 200 mV (below OCP) and 400 mV (above OCP).

From the extrapolation of Tafel slopes at the polarization curves were determined the corrosion potential (E_{corr}), corrosion current (i_{corr}), polarization resistance (R_p) and the protection efficiency (PE) for samples studied. PE of the coatings was determined for the equation, where i_{corr} and i_{corr}^* are the corrosion current densities obtained for uncoated and coated substrates, respectively:

Table 1. Description of the samples

Sample	Description
F1A60M	Tinplate coated with hybrid film with 0.5% diisodecyl adipate plasticizer addition
F2A60M	Tinplate coated with hybrid film with 1% diisodecyl adipate plasticizer addition
F3A60M	Tinplate coated with hybrid film with 2% diisodecyl adipate plasticizer addition
F4A60M	Tinplate coated with hybrid film with 4% diisodecyl adipate plasticizer addition
F5A60M	Tinplate coated with hybrid film without plasticizer addition
FI	Uncoated tinplate

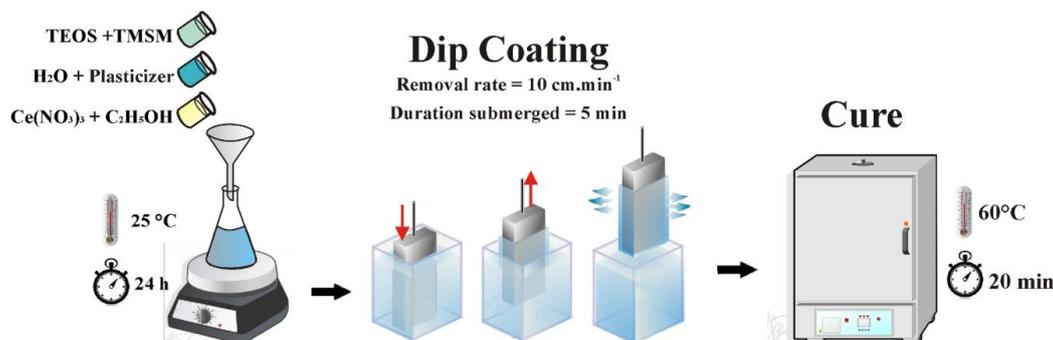


Figure 1. Schematic representation of coating elaboration.

$$PE = 100 \frac{i_{\text{corr}} - i_{\text{corr}}^*}{i_{\text{corr}}}$$

For the EIS measurements, the samples were available up to 96 h and the systems were monitored by open circuit potential (OCP) for 1 h prior to each test. The amplitude of the EIS perturbation signal was a sinusoidal 10 mV (rms) signal, and the frequency range was from 100 kHz to 10 mHz using a Nova[®] frequency response analyzer and a Autolab PGSTAT 30 potentiostat. The results obtained were fitted using electrical equivalent circuits (EEC) using the Nova[®] software. The consistency of the experimental data was verified with the Kramers-Kronig transform (KKT), and data that did not match were discarded.

RESULTS AND DISCUSSION

Morphological characterization

SEM micrographs were performed for the hybrid films with plasticizer addition F1A60M (0.5% plasticizer), F2A60M (1% plasticizer), F3A60M (2% plasticizer) and F4A60M (4% plasticizer), and the hybrid film without plasticizer addition F5A60M before the electrochemical tests. They analyses are shown in Figure 2.

The micrographs show that the hybrid films with less diisodecyl adipate plasticizer concentration F1A60M and F2A60M (0.5 and 1%) were the only samples to show cracks and the F4A60M sample shows discontinuities in the film surface.

The presence of cracks in the films with a low concentration of plasticizer was due to silane precursors TMSM and TEOS that tend to form a compact tridimensional network and, due the presence of the plasticizer, the latter is encapsulated in the network due to the interaction forces (*i.e.*, hydrogen bonds, van der Waals forces or covalent bonds). Thus, branch mobility was limited, due to the absorption of mechanical energy. This produces a more rigid and fragile hybrid film. The phenomenon is known as anti-plasticizing [33]. The presence of discontinuities in the film with the highest concentration of plasticizer can be associated with incompatibilities between sol and plasticizer. According to Grossman *et al.* [34], adipate plasticizers typically are used from C7 to C10 and heterogeneities can rise when the plasticizer is added in higher concentrations for a higher number of carbons. As TEOS is a C₈ and TMSM is a C₁₀ molecule, this explanation accounts for the discontinuities observed in Figure 2 (F4A60M).

The increase in thickness of the films with the addition of diisodecyl adipate could be due the plas-

ticizer, which enters into polymeric chains, thus increasing their free volume. Adipates are external plasticizers; *i.e.*, they are additives that interact physically with the polymer. There can be weak attractive force between the polymeric matrix of the film and the plasticizer, through weak force as hydrogen bonds and/or van der Waals forces, though adipates do not react chemically with the silane precursor radical. Due to its smaller molecular size compared with the polymeric matrix of the film, diisodecyl adipate promotes an increase in mobility of the film, flexibility of the molecules, attributed to the generated increase of free volume, enabling an increase in the layer thickness for those systems.

The thickness of the hybrid film layer was determined from a cross-section SEM image analysis (Figure 2) and these results are shown in Table 2. As can be observed, all hybrid films with diisodecyl adipate addition (F1A60M, F2A60M, F3A60M and F4A60M) showed a significant layer thickness increase, compared to the sample without plasticizer addition (F5A60M). The F1A60M and F2A60M hybrid films had the higher layer thickness values; however, they also exhibited cracks (Figure 2).

However in this study, it was observed that the hybrid films with low plasticizer concentration presented higher layer thickness values, but also exhibited cracks (Figure 2). This was due to the fact that, despite of the adipate plasticizers being external plasticizers, *i.e.*, that they only interact physically with the polymer; this additive is esterificated by the adipic acid after esterification, and hence they pertain a reactive group. A problem that can rise with such reactive groups is that they can react with the polymeric matrix of the coating, making the film molecular size bigger, thereby reducing its flexibility [35], and promoting crack formation.

The results of the contact angle measurements for the different systems studied are shown in Table 2. According to the results, all of the hybrid films showed hydrophilic behavior and there were no significant differences among the contact angle values for the systems. The samples were hydrophilic in nature and there was not a significant difference among the contact angle values for the systems, because the diisodecyl adipate plasticizer is not involved in the silane hydrolysis and condensation reactions. The predominant interactions between the plasticizer and the polymeric matrix are hydrogen bonds or van der Waals forces, which are weak interactions and do not interfere in film formation.

Silane precursor-based hybrid films show hydrophobic behavior when they are not sufficiently cross-

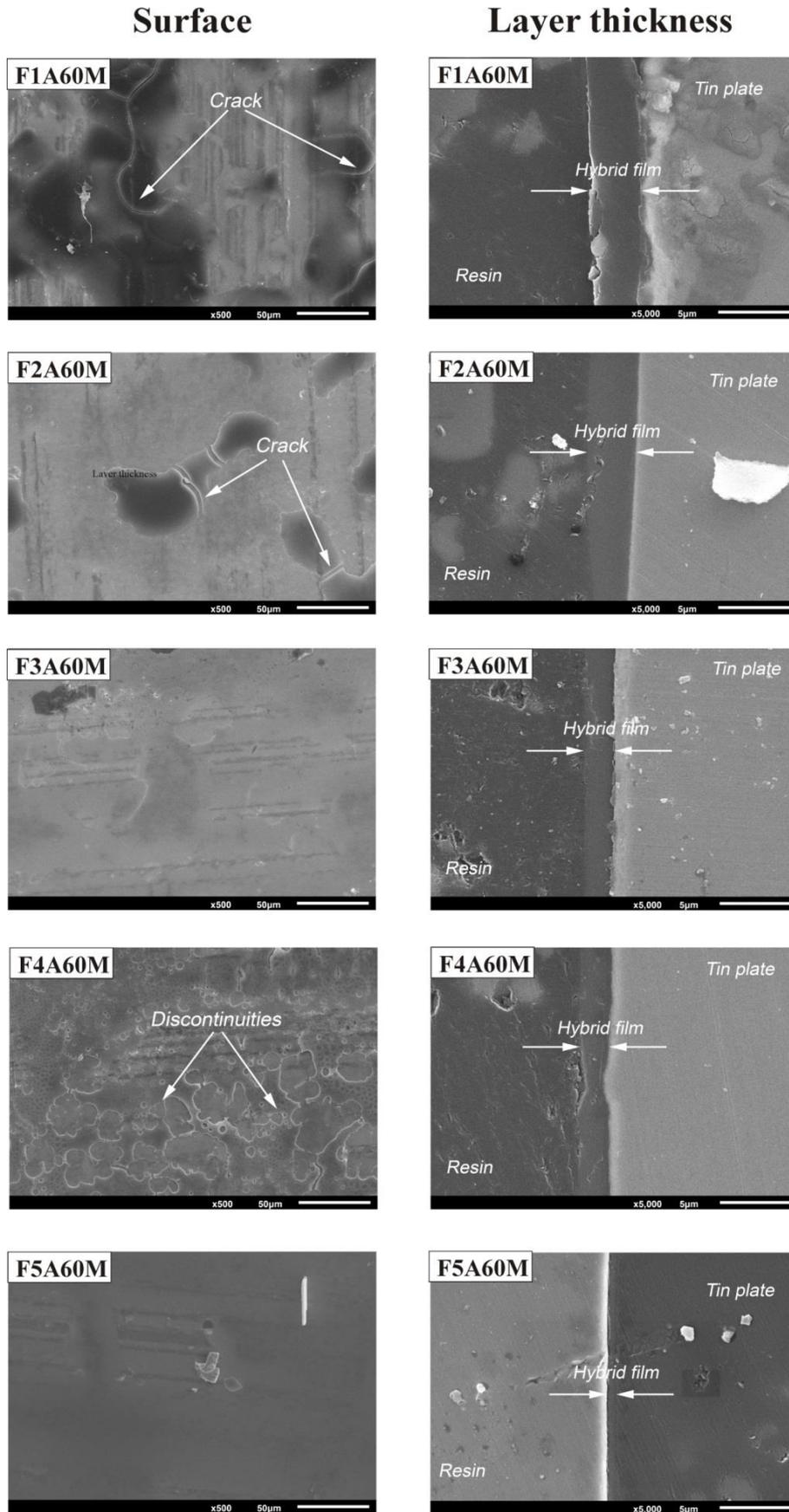


Figure 2. SEM images and layer thickness of the hybrid films.

Table 2. Layer thickness, contact angle and surface roughness values for the hybrid films studied

Sample	Layer thickness, μm	Contact angle, $^\circ$	Surface roughness		
			R_a / μm	R_{rms} / μm	Peak-to-peak, μm
F1A60M	3.93±0.31	72±1.09	0.37±0.09	0.47±0.08	4.41±0.16
F2A60M	3.21±0.36	77±0.72	0.36±0.11	0.48±0.10	3.91±0.13
F3A60M	1.96±0.18	76±0.87	0.31±0.08	0.39±0.09	4.11±0.11
F4A60M	2.14±0.24	66±0.60	0.34±0.09	0.43±0.08	2.57±0.09
F5A60M	0.63±0.11	78±1.50	0.41±0.12	0.50±0.11	3.53±0.12
FI	-	73±1.90	0.43±0.10	0.51±0.10	2.40±0.11

-linked. During the curing process, siloxane bonds form a network that hinders water penetration, consequently enhancing the hydrophobic character. Hence, the contact angle for a highly cross-linked film is about 90° . Neither silane precursors hydrolysis nor cross-linking (polycondensation) are completed during curing at 60°C [36]. Subsequently, therefore, non-hydrolyzed ester and hydrophilic -OH groups are present in the hybrid films structures and favor water absorption [37].

All of the studied hybrid film samples contained Ce in their formulation and in accordance with a literature survey performed by Palomino *et al.* [38], the results suggest that this behavior was due to the joint action of two factors: *i*) improved barrier properties imparted to the silane film due to the incorporation of silica particles, which would block preferential pathways for electrolyte penetration, *ii*) the higher degree of polymerization and increased thickness of the silane layers, due to the presence of cerium ions. The direct influence of Ce can be observed in the results of contact angle for F5A60M sample (without plasticizer) where the presence of Ce promoted the formation of a more hydrophobic film than was the case with the other films.

Roughness values are summarized in Table 2, where R_a stands for arithmetic average, R_{rms} for average square roughness, and R_y for maximum rough-

ness or peak to trough size. There was no evident consistent variation in the roughness values, due to the low resolution capability of the technique (*i.e.*, a variation of only micrometers). However, all of the hybrid films with plasticizer addition showed better roughness values compared to the F5A60M sample (without adipate) and to uncoated tinplate.

Electrochemical characterization

Open circuit potential (OCP) monitoring was conducted in a 0.05 mol L^{-1} NaCl solution to verify the potential variation with time. These results are shown in Figure 3a. Also, polarization curves for all the systems are presented in Figure 3b. From Tafel slope extrapolations (Table 3), the corrosion current density (i_{corr}), corrosion potential (E_{corr}) and polarization resistance (R_p) values were determined.

Open circuit potential values (Figure 3a) for 1 h of immersion indicate that all hybrid films had potentials shifted upwards in relation to the uncoated tinplate (FI), in the following order: F1A60M (-390 mV) > F4A60M (-440 mV) > F5A60M (-448 mV) > F2A60M (-450 mV) > F3A60M (-468 mV) > FI (-509 mV); that is, the hybrid films presented less active potentials and promoted the formation of a barrier between the substrate and the medium.

Furthermore, the potential for the F1A60M system shifted in the positive direction (-390 mV) com-

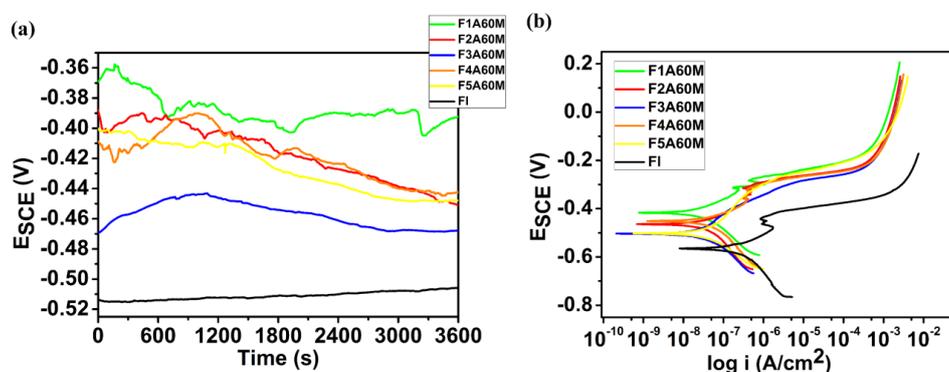


Figure 3. a) Open circuit potential and b) polarization curves in a 0.05 mol L^{-1} NaCl solution for all studied hybrid films and for tinplate substrate.

Table 3. Obtained data from Tafel extrapolation

Sample	$i_{\text{corr}} / \text{mA m}^{-2}$	$E_{\text{corr}} / \text{mV}$	$R_p / \Omega \text{ m}^2$	PE / %
F1A60M	0.566	-417	72.5	98.80
F2A60M	0.574	-464	56.0	98.78
F3A60M	0.914	-504	73.2	98.06
F4A60M	0.778	-451	42.1	98.35
F5A60M	0.570	-497	68.0	98.79
FI	47.1	-581	0.554	-

pared to the uncoated tinplate sample FI (-509 mV); *i.e.*, this difference in potential value results from a barrier effect from the hybrid film [39]. Moreover, the equilibrium potential that was observed for the tinplate substrate after 1 h immersion (-509 mV *vs.* SCE) is associated with the formation of a Sn(II)-oxide/hydroxide layer [40,41].

With regard to the polarization curves (Figure 3b), it is observed that all of the hybrid films (F1A60M, F2A60M, F3A60M, F4A60M and F5A60M) showed a decrease (two orders of magnitude) in the corrosion current density (i_{corr}) in comparison with the uncoated tinplate sample, which denotes the protective action of those films. The polarization curves also showed an increase by almost one or two orders of magnitude in terms of the polarization resistance value (Table 3).

Analyzing the hybrid films only, the siloxane-adipate film obtained with a 2% concentration of diisodecyl adipate, which corresponds to the sample F3A60M ($i_{\text{corr}} = 0.914 \text{ mA m}^{-2}$ and $R_p = 73.2 \Omega \text{ m}^2$) showed the best performance of the studied hybrid films, yet only marginally so.

From the polarization curves it can be observed that the tinplate substrate showed higher values of current density ($i_{\text{corr}} = 47.1 \text{ mA m}^{-2}$) and a lower polarization resistance ($R_p = 0.554 \Omega \text{ m}^2$) compared to the studied hybrid films.

From polarization tests showed that all of the hybrid films exhibited better protective performance than the sample without a hybrid film. This occurs due to the covalent bonds of the organic and inorganic precursors, demonstrating the synergistic effect of the TMSM and TEOS precursors' presence in the hybrid film.

Of the hybrid films, the sample with 2% plasticizer performed better, due to the presence of weak bond strength between the plasticizer and the silane precursors radicals and the increased layer thickness. However, the film was more rigid and fragile [35].

The poor performance of uncoated tinplate could be related to the presence of tin oxide/hydroxide that partially passivates the metallic surface. The passivity breakdown at -430 mV *vs.* SCE is related to

pitting attack that is induced by the chloride effect [42]. Galic [43] suggests that the adsorption of chloride ions at the oxide-electrolyte interface leads to the formation of a tin-oxychloride film, with less protective behavior.

Nyquist and Bode plots obtained by electrochemical impedance spectroscopy tests for 24 and 96 h of immersion in 0.05 mol L^{-1} NaCl solution for all the studied systems and for tinplate are shown in Figure 4. Table 4 shows the R_{HF} (resistance for high frequency) and R_{CP} (resistance caused by corrosion process).

The impedance results obtained from the Nyquist plot (Figure 4) show higher resistance values for the sample F3A60M ($R_{\text{HF}} = 472 \text{ k}\Omega \text{ cm}^2$) after 24 h of immersion. This is due to the fact that these coatings had no cracks or discontinuities, as was observed on the SEM images (Figure 2). However, after 96 h of immersion the resistance for the system F3A60M ($R_{\text{HF}} = 312 \text{ k}\Omega \text{ cm}^2$), the resistance diminished by a factor of two. Furthermore, the F3A60M sample showed a higher phase angle (around 68° - Figure 4) and a higher impedance modulus (around $\log |Z| = 5.25$ - Figure 4) values, after 96 h of immersion.

On the other hand, the F1A60M sample, which had a high layer thickness and had the addition of 0.05% plasticizer showed lower resistance values after 24 ($R_{\text{HF}} = 92.71 \text{ k}\Omega \text{ cm}^2$) and 96 h ($R_{\text{HF}} = 4.31 \text{ k}\Omega \text{ cm}^2$) of immersion. These reveal the fragility of this coating, with cracks that allow permeation of the electrolyte through the film and towards the substrate.

The EIS tests results indicated that the good electrochemical performance with 2% of diisodecyl adipate plasticizer occurs because the plasticizer concentration is the most suitable to increase the free volume, allowing the movement of the polymeric chain and giving flexibility to the organic radicals bound to the silicon atom. Also, plasticizer inclusion avoids interactions between the organic radicals in the silane precursors, enhances the mobility of the chain extremities and improves the flexibility of the system.

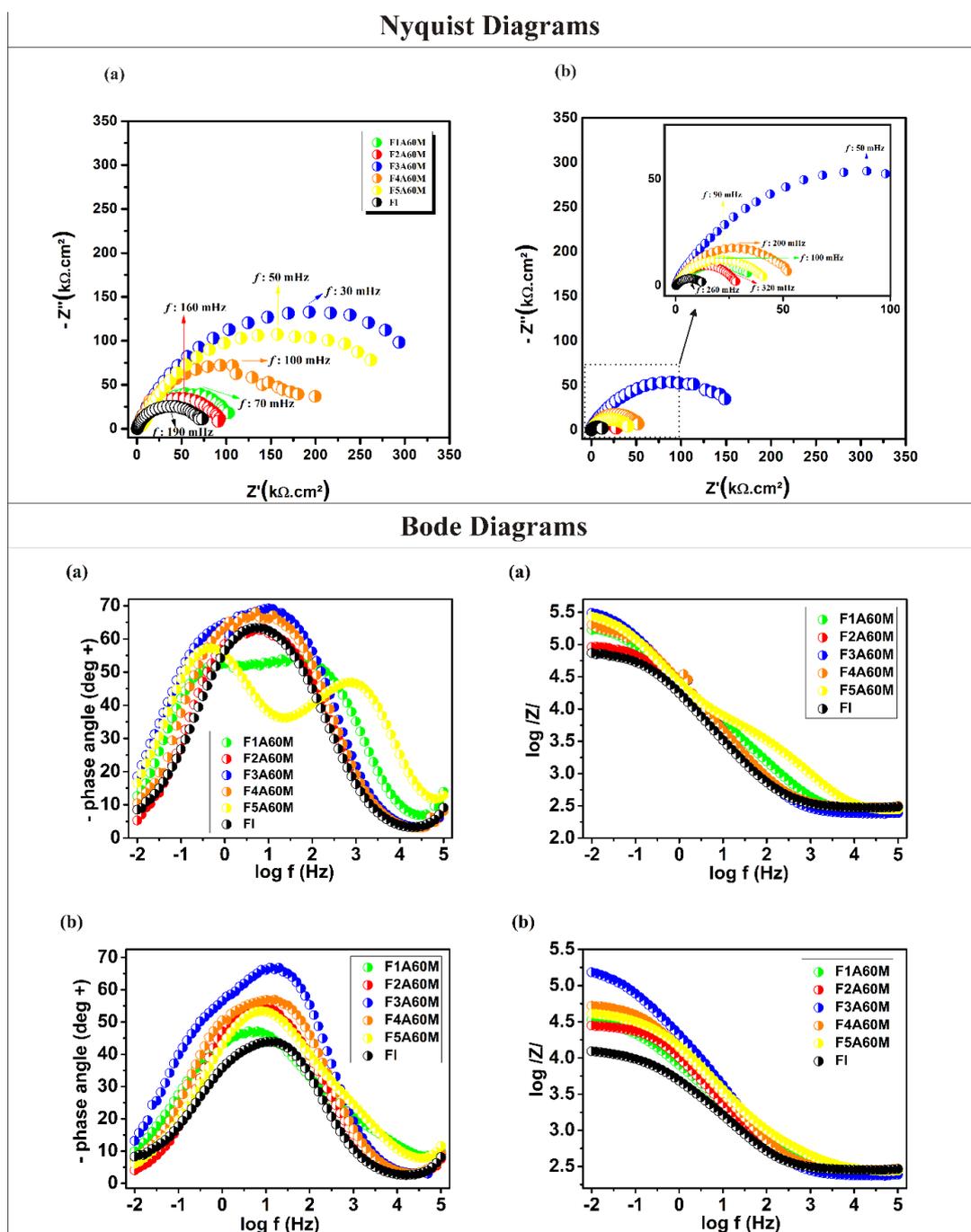


Figure 4. Nyquist and Bode plots obtained for hybrid film coated and uncoated tinplate in NaCl 0.05 mol L⁻¹ solution for: a) 24 and b) 96 h of immersion.

EIS tests also revealed the poor performance of the hybrid film with less plasticizer concentration. Although the formulation of these systems has promoted an increase in the layer thickness (Figure 2 and Table 2) due to the plasticizer addition, a weak and porous structure resulted, due to the formation of intertwined molecules linked only weak bonds (hydrogen bonds). Moreover, it restricted the mobility of small branches in the chain, causing cracks on the

films, which contribute to the poor corrosion resistance of these samples and their consequent inability to resist long periods of immersion.

It was observed that after 96 h of immersion the hybrid films showed a decrease in their protective action, which reduced their efficiency in the corrosive environment. This behavior was due to the permeability of the film, which occurred during the test and reduced the barrier properties of the film [44].

Equivalent circuit models can be used to explain the electrochemical impedance data obtained from the EIS tests. These models, which use a combination of resistance, capacitance and other electrical elements to simulate the coating response, can be helpful in providing a clear understanding of the response of the electrochemical system [45]. In this work, two equivalent electrical circuit models were used (Figure 5). In several circuits, the capacitance was substituted by a CPE in order to accommodate the non-ideality of the systems. In these circuits (Figure 5a), R_e represents the electrolyte resistance, R_{HF} represents the film resistance and CPE_{HF} represent film capacitance for high frequency. The same equivalent circuit model (Figure 5a) is proposed for the electrochemical behavior simulation for all immersion times studied (1, 24, 48, 72 and 96 h) for the F2A60M, F3A60M and F4A60M samples. This behavior was observed by the other authors [46,47], indicating that the hybrid films retard the corrosion processes on the tin plate surface.

Table 4 presents the equivalent electrical parameter obtained by fitting the equivalent circuit from the EIS test data, obtained for the F1A60M, F2A60M, F3A60M, F4A60M and F5A60M hybrid films after 96 h of immersion in a 0.05 mol L^{-1} NaCl solution. The percentage errors shown in brackets in Table 4 show that the errors involved in the fitting procedure were less than 10% (less than 5% in most cases).

The other equivalent circuit model (Figure 5b) was proposed for the electrochemical behavior simulation at all immersion times studied (1, 24, 48, 72 and 96 h) for the F1A60M and F5A60M samples [40,41]. This new equivalent circuit model was employed because the other circuit equivalent (Figure 5a) does not allow approximation between simulation and real data. In these circuits (Figure 5b), R_e represents the electrolyte resistance, R_{HF} represents the film resistance and CPE_{HF} represent film capacitance for high frequency, R_{CP} and CPE_{CP} represent the resistance and a constant phase element indicating the diffusion of electrolyte through the film, initiating the

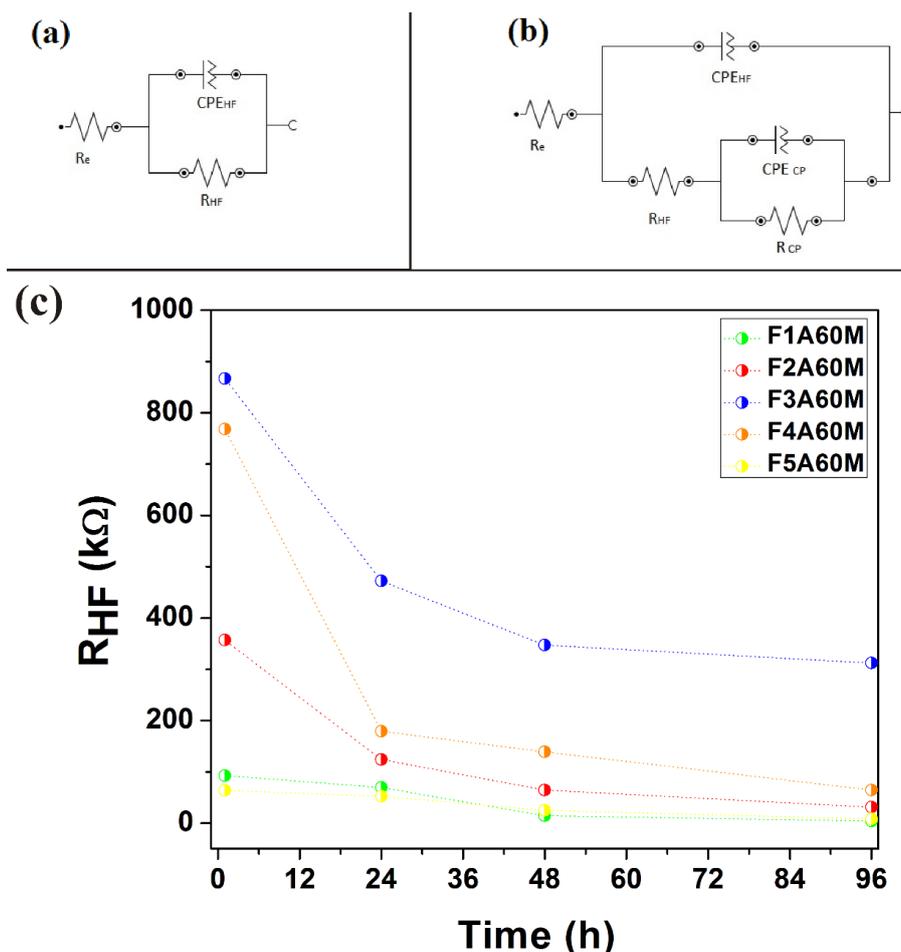


Figure 5. Equivalent electrical circuits for EIS data fitting (a,b) and evolution of the hybrid films resistance for F1A60M, F2A60M, F3A60M, F4A60M and F5A60M in a 0.05 mol L^{-1} NaCl solution with the immersion time (c).

Table 4. Electrical elements fitted values for the samples up to 96 hours of immersion in 0.05 mol L⁻¹ NaCl solution. The error percentage associated with each parameter value is given in parenthesis

Time, h	$R_e / \Omega \text{ cm}^2$	$R_{HF} / \Omega \text{ cm}^2$	$CPE_{HF-Q} / \mu\text{F cm}^2$	CPE_{HF-n}	$R_{CP} / \Omega \text{ cm}^2$	$CPE_{CP-Q} / \text{nF cm}^2$	CPE_{CP-n}	$\chi^2 \times 10^3$
F1A60M								
1	202 (5.7)	92.71 (3.4)	3.29 (5.1)	0.73 (5.8)	134 (5.6)	9.77 (5.7)	0.51 (6.2)	0.79
24	184 (2.7)	69.5 (3.9)	3.69 (4.9)	0.44 (1.4)	89.7 (5.2)	11.4 (2.8)	0.73 (1.5)	1.32
48	167 (2.1)	14.53 (3.5)	4.01 (1.3)	0.41 (3.4)	69.7 (1.2)	13.3 (1.2)	0.69 (0.6)	0.87
96	132 (3.1)	4.31 (5.1)	4.47 (4.2)	0.39 (1.9)	41.8 (1.4)	14.9 (0.4)	0.64 (0.5)	0.95
F2A60M								
1	234 (1.7)	357 (2.3)	3.09 (1.8)	0.76 (0.6)	-	-	-	3.17
24	201 (0.8)	124 (1.9)	3.45 (1.4)	0.72 (0.5)	-	-	-	4.71
48	189 (0.6)	64.7 (1.9)	3.73 (1.7)	0.69 (0.2)	-	-	-	2.98
96	166 (0.8)	31.1 (1.2)	3.99 (1.1)	0.66 (0.3)	-	-	-	3.47
F3A60M								
1	293 (4.1)	867 (2.5)	0.11 (2.1)	0.84 (1.4)	-	-	-	2.93
24	271 (1.9)	472 (3.7)	0.51 (1.4)	0.81 (0.6)	-	-	-	3.56
48	243 (1.7)	347 (3.9)	1.31 (1.9)	0.79 (0.3)	-	-	-	3.02
96	229 (2.1)	312 (4.2)	2.73 (2.4)	0.76 (0.7)	-	-	-	3.93
F4A60M								
1	241 (3.1)	768 (5.7)	2.81 (3.7)	0.78 (0.6)	-	-	-	1.07
24	211 (1.3)	179 (2.7)	2.93 (2.9)	0.73 (0.3)	-	-	-	1.15
48	197 (0.6)	139 (0.8)	3.12 (0.9)	0.71 (0.4)	-	-	-	0.79
96	171 (1.5)	64.7 (3.3)	3.64 (2.3)	0.70 (0.3)	-	-	-	0.69
F5A60M								
1	207 (2.2)	63.7 (4.9)	3.61 (4.7)	0.69 (5.4)	912 (4.8)	9.33 (3.2)	0.71 (3.9)	5.31
24	159 (3.5)	52.37 (4.4)	3.94 (5.8)	0.64 (3.8)	287 (3.1)	11.26 (2.7)	0.76 (3.9)	4.39
48	137 (3.1)	24.74 (5.2)	4.42 (5.4)	0.60 (6.6)	146 (4.4)	12.88 (4.1)	0.71 (4.1)	3.27
96	112 (2.9)	8.51 (3.5)	4.89 (2.6)	0.54 (2.2)	61.9 (2.7)	13.86 (2.1)	0.63 (3.4)	2.94

corrosion process [17,41,48,49]. The same equivalent circuit model (Figure 5b) was proposed for the electrochemical behavior simulation at all immersion times studied (1, 24, 48, 72 and 96 h) for the F1A60M and F5A60M samples. This model is consistent with the protective action lower of these systems. The system resistance values are found to be around ($R_{HF} = 4.31 \text{ k}\Omega \text{ cm}^2$ for F1A60M and $R_{HF} = 8.51 \text{ k}\Omega \text{ cm}^2$ for F5A60M) after the 96 h of immersion (Table 4).

Table 4 shows that the sample F3A60M had lower capacitance values than the other analyzed samples until the end of the test ($CPE = 11.89 \mu\text{F cm}^2$), denoting the best protective barrier properties of the hybrid film. Furthermore, there was an increase in the coating capacitance of the F1A60M sample after 1 hour of immersion ($CPE = 3.29 \mu\text{F cm}^2$, Table 4) and after 24 h of immersion ($CPE = 3.69 \mu\text{F cm}^2$, Table 4).

For the samples F2A60M, F4A60M and F5A60M, a slight increase capacitance values (Table 4) was observed in the mean 48 h for 96 h immersion. After 96 h of immersion, another small significant increase in the capacitance of the film was observed.

The film capacitance always tends to increase with immersion time as result of electrolyte uptake. This behavior is due to a significant increase of the dielectric constant of the coating, which is influenced strongly by electrolyte penetration into the coating. Moreover, chi-square (χ^2) was introduced in Table 4 and the observe values were around 10^{-3} , similar to results obtained for Sakai *et al.* (2012) [40].

Figure 5c shows the evolution of the coating properties (*i.e.*, the resistance) as a function of immersion time. The F3A60M ($R_{HF} = 867 \text{ k}\Omega \text{ cm}^2$) sample exhibited the highest resistances for 1 h immersion. Furthermore, the F3A60M sample exhibited the highest resistances at all immersion times. The resistance all of the coatings decreases slowly over an immersion time of 96 hours, which reflected the stability of the coating [18].

The evolution of a coating resistance is a major characteristic of the barrier properties of a protective layer. Generally, the resistance values decreased during the first hours of immersion, due to the development of conductive pathways inside the film. The

high resistance of the sample with 2% plasticizers should be due to the increasing the ability of polymer chains to slide over one another; that is to say, the chain movement enhances the flexibility of the organic radicals that are bound to the silicone atoms.

Figure 6 shows images for all of the hybrid films after 96 h of the electrochemical impedance tests. Hybrid films with higher plasticizer concentrations (F3A60M, Figure 6c and F4A60M, Figure 6d) were observed to have developed less corrosion products after the electrochemical tests, confirming the impedance results.

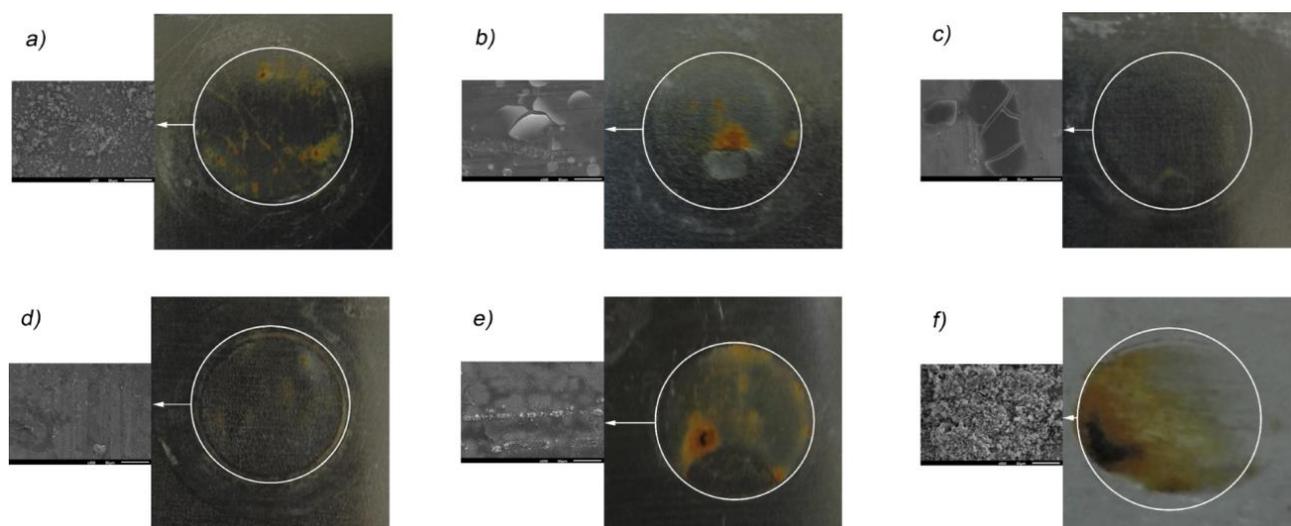


Figure 6. SEM images of the samples: a) F1A60M, b) F2A60M, c) F3A60M, d) F4A60M, e) F5A60M and f) FI after 96 h of immersion in NaCl 0.05 mol L⁻¹.

Red corrosion products were observed on the electrode surface at the end of the experiments, indicating the formation of iron oxides. For hybrid films without plasticizer (Figure 6e) and with lower plasticizer concentrations F1A60M (Figure 6a) and F2A60M (Figure 6b), abundant and more localized red corrosion products were observed on their surfaces, which were considered to be iron oxides.

CONCLUSION

The obtained results are sufficient to state that all hybrid film coatings shifted potentials indicating less activity, and diminished the corrosion current densities (i_{corr}) in relation to the uncoated tinplate (FI), evidencing the protection provided by the films. The hybrid film with 2% of diisodecyl adipate showed the best performance in the electrochemical impedance spectroscopy tests.

Films with concentrations lower than 2% plasticizer were thicker, brittle and permeable, which decreases the effect barrier. Films with concentrations

greater than 2% plasticizer featured lower thickness, irregularities and cracks in the surface, which decreases its efficiency as a barrier film.

Therefore, the addition of 2% of diisodecyl adipate on the silane film improved the morphological and electrochemical properties of the film, when compared to the film without plasticizer. These results indicate that this film is a viable alternative to protect the tinplate against corrosion.

Acknowledgments

This work was done with the financial support of CAPES, a Brazilian government agency for the human resources development. Authors would also like to acknowledge the financial support of CNPq and FAPERGS, and the Centre for Electron Microscopy of the Federal University of Rio Grande do Sul for the SEM analysis.

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NAUČNI RAD

UTICAJ KONCENTRACIJE DIIZODECIL-ADIPATA U HIBRIDNIM FILMOVIMA NANETIH NA LIMU

Hibridni filmovi na bazi siloksana su krhki i male mehaničke čvrstoće zbog njihovih osobina staklastog materijala. Stoga je razvijena jedna nova formulacija koja uključuje plastifikator u cilju povećanja debljine nanosa uniformnog i homogenog hibridnog filma na limu, i obezbeđenja fleksibilnosti polimernog matriksa. Limene ploče su obložene hibridnim filmom dobijenim sol-gel postupkom, uz dodatak alkoksidnih prekursora 3-(trimetoksisilil) propil metakrilat i tetraetokasilan, kao i 0,01 mol/dm³ cerijum nitrata. Ocenjivan je uticaj koncentracije plastifikatora di-isodecil adipata. Filmovi su okarakterisani skenirajućim elektronskim mikroskopom, profilometrijom, merenjem potencijala otvorenog kola, polarizacionim merenjima i spektroskopijom elektrokemijske impedancije. Rezultati su pokazali da su svi filmovi sa di-isodecil adipatom imali veću elektrokemijsku performansu u odnosu na nepremazan lim. Međutim, film sa koncentracijom plastifikatora od 2 % je imao najbolju performansu u elektrohemijskim testovima, iako je imao manju debljinu.

Ključne reči: hibridni film, diizodecil-adipat, beli lim, elektrohemijsko ponašanje.