Corrosion Resistance of Tin plate Substrates due to Organic or Inorganic Acid Hydrolysis of Siloxane-poly(methyl methacrylate) Hybrid Films

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Introduction
Pretreatments of metal surfaces based on siloxane-PMMA have demonstrated promising results, attracting attention of industries. These hybrid films improve corrosion resistance [1] and adhesion of organic layers. Besides, they reduce environmental impacts compared to the chromatization process [2]. Moreover, siloxane-PMMA hybrid films promote an excellent anchorage on metallic surface [3-4] for posterior paint application [5]. The sol-gel films adhesion to the substrate and corrosion protection rely on the chemically inert barrier they interpose between metal and aggressive environment. To carry out the coating, the sol-gel solution is prepared by hydrolysis and condensation of appropriate metal alkoxides: M(OR)n, R representing an organic group and M a metal [6]. The sol-gel process has successfully been utilized to prepare silicate gels by hydrolyzing tetrafunctional alkoxide precursors employing acid as a catalyst [7]. The overall process involves hydrolysis and condensation reactions which lead to the growth of clusters that eventually colloid and link together to form a gel. The structure of the gel and the kinetics of aggregation have been object of studies [8,9]. The aim of this work is to study and compare the effect of acetic and hydrochloric acid addition on the corrosion resistance provided by the hybrid films to tinplate.

Experimental
The tinplate substrates (2cm×6cm) were degreased ultrasonically in acetone and rinsed with distilled water. The hybrid films were obtained on the substrate from a sol constituted by the silane precursors: γ-methacryloxypropyl-trimethoxysilane (TMSPMA – C10H20O3Si) and tetraethoxysilane (TEOS – C8H20O4Si) with addition of methyl methacrylate (MMA). The hydrolysis/polycondensation reaction involving the silicon alkoxide was performed by mixing water, acidified with acetic (CH3COOH) or with hydrochloric (HCl) acids to pH = 3, to the solution of TEOS and TMSPMA added in ethanol maintained at 60 °C for 1 hour. This inorganic phase precursor solution was stirred for 1h. The organic phase was performed in a separate recipient, where MMA and benzoyl peroxide (BPO) were mixed and stirred, at room temperature, until total homogenization of BPO. The contents of the two recipients were then mixed and stirred for 5 minutes, at 45°C, forming a transparent sol in which the tinplate samples were immersed. The elaboration of the hybrid films was performed by the dip-coating process with a withdrawal speed of 14 cm.min⁻¹. The samples were air-dried for approximately 10 minutes. This process was repeated 3 times. Afterwards, the coated substrates were heated at 55°C for 24 h, and cured at 160°C for 3 h.

Experimental techniques. Scanning electron microscopy (SEM) (JEOL-JSM 5800) with an acceleration voltage of 20 keV was used to evaluate the film thickness on cross sections. The anticorrosion performance of the coatings was evaluated by open circuit potential (EoCP) monitoring, polarization curves and electrochemical impedance spectroscopy (EIS) measurements in a 0.05M NaCl solution. A three-electrode cell was used to perform the analyses, with a platinum wire as counter electrode and SCE as the reference electrode. The working electrode area was 0.626 cm². The EIS measurements were done after different times until 96 hours, The amplitude of the EIS perturbation signal was 10mV, and the frequency...
range studied was from 100 kHz to 10 mHz using a Solartron 1255 frequency response analyzer and a potentiostat PAR273.

Results and Discussion
Morphological characterization. The thickness layer was determined by cross section images (Figure 1). The thickest film was that of siloxane-PMMA with HCl (Figure 1-b) which had a thickness value of 3.7±0.3µm i.e. two times the layer thickness found for the acetic acid-containing film of 1.6±0.3µm (Figure 1-a). It can be related to the fact that HCl is a strong acid, undergoing substantially complete ionization when in aqueous solution even at high concentrations. Since the ionization of the acid is substantially complete and the polarity of the system is increased, the release of ions to the reactions is facilitated improving their rate and resulting in an important increase of the layer of siloxane-

![Hybrid film](image1)

**Fig. 1.** Cross section micrographs obtained by SEM of hybrid films (a) acetic and (b) hydrochloric acid.

Electrochemical characterization. From EOC values and polarization curves (Fig. 2-a and Fig. 2-b) it is observed that coating tin plate with hybrid films displaces its corrosion potential values in positive direction while decreasing cathodic and anodic current density. This must be related to the barrier layer between substrate and the electrolyte provided by the hybrid films. It was not observed an important difference between the hybrid films obtained with acetic acid or hydrochloric acid addition into the sol.

![Polarization curves](image2)

**Fig. 2.** (a) Open-circuit potential (EOC) and (b) polarization curves of covered and bare tinplates in NaCl 0.05 M solution.

Error! Fonte de referência não encontrada. shows EIS Bode diagrams for the hybrid films obtained with acetic or hydrochloric acid after 24, 48, 72 and 96 h of immersion in a 0.05 M NaCl solution. The Bode phase angle diagrams show for all times studied a well defined time constant in the higher frequencies range for hybrid films obtained with the acetic acid added into the sol, associated to the barrier film resistance. This fact may be related to the acetic acid being an organic acid having a low degree of ionization, ie, the molecules are not very much ionized, making it impossible to promote a reaction with the NaCl electrolyte therefore maintaining the pH 3 by its buffering capacity and consequently enhancing the corrosion resistance (Fig. 4-a). For the hydrochloric acid added into the sol it is observed for all times studied a well defined time constant in the medium to low frequency range, indicating an acceleration of the interfacial process associated with the tin oxides on the substrate surface. This could be explained by the exposition to the saline solution with a strong degree of dissociation (Na⁺ + Cl⁻), what enhances the strength of the hydracid causing accelerated corrosion and consequently destroying the siloxane-PMMA layer (Fig.4-b).
Fig. 3. Bode diagrams: (a) 24 h, (b) 48 h, (c) 72 h and (d) 96 h in the NaCl 0.05M immersion.

Fig. 4. Coated samples after 96 hours immersion in 0.05 M NaCl: (a) acetic acid and (b) hydrochloric acid.

Conclusions
The results highlighted the improved protective properties of the siloxane-PMMA films on tin plates, denoting the anticorrosion action of these coatings. Besides, it was shown that the acetic acid in the formulation even promoting a thinner layer than the hydrochloric acid, determined the best efficiency of the anticorrosion properties in a 0.05 M NaCl solution.

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