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Electrochemical behavior of organic/inorganic films applied on tinplate in different aggressive media

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ABSTRACT

The corrosion behavior of bare and coated tinplate samples was investigated using two different electrolytes: 0.1 M NaCl and 0.1 M citric acid/sodium citrate buffer solutions. A hybrid sol–gel film was synthesized to coat the tinplate samples. The study was performed by polarization and electrochemical impedance spectroscopy techniques. The morphology characterization was made by scanning electron microscopy, energy dispersive X-ray, X-ray diffraction and mechanical profilometry techniques.

The obtained results indicate that the corrosion resistance is strongly dependent on the electrolyte. Better behavior is observed for samples in contact with chloride ions, even though at the end of the experiment numerous pits are observed all over the surface. Samples immersed in the citric/citrate solution undergo severe attack, which can be associated with a faster tin dissolution in presence of citrate ions.

1. Introduction

Tinplate is a cold-rolled, low carbon thin steel plate, coated on both sides with pure tin. Tinplate cans are extensively used in the food packaging industry, when mechanical robustness and withstanding at sterilization temperatures are required. Tinplate combines in one material the strength of steel and the corrosion resistance and good appearance of tin [1]. However, tinplate cans in corrosive food media may present problems, such as corrosion failures, loss of seal integrity, and damage in the appearance product that can affect the nutritional value of the canned food. During the corrosion process, foodstuff can be contaminated by tin, even though it is not considered as a poisonous metal, very large dose can produce serious digestive disturbances [1,2]. Thus, during the manufacturing process, it is necessary to apply passivation treatments that improve corrosion resistance and adhesion of the lacquer coating finishing. The passivation treatments also help in preventing the tin oxide growth. Nowadays, the chromate passivation treatment is widely used in the tinplate industry, due to the excellent protecting behavior provided. Nevertheless, chromate is highly toxic and carcinogenic, therefore, new alternative pre-treatments more environmentally friendly have been proposed recently [3–6].

In addition, the use of organic coatings applied on tinplate is a generalized procedure employed to improve the corrosion resistance when the cans are in contact with aggressive food products. The lacquers based on epoxy resins are the most widely employed, due to the good barrier properties [7–10]. One constituent employed in the manufacture of epoxy resins is the monomer BADGE (Bisphenol A diglycidyl ether). BADGE is listed as an IARC (International Agency for Research on Cancer) Group 3 carcinogen, meaning it is "not classifiable as to its carcinogenicity to humans" [11]. Nevertheless, the new legislations are bounded on the use of BADGE precursors. Consequently, the development of new more ecological lacquers formulations is an utmost requirement. The use of inorganic or organically modified inorganic materials (hybrid films) obtained by sol–gel technology represents a compliant alternative. They have been successfully used to improve the corrosion resistance of several metallic substrates [12–15]. Nevertheless, their use is scarce with tinplate substrates [16–18], maybe because of the complexity of the metal/coating/food system. The tinplate used in canning industry is a heterogeneous and stratified structure. The material is submitted to a heat treatment to obtain a $FeSn_2$ alloy, which increases the corrosion resistance of the system. On the other hand, the food products play an important role because, depending on their physico-chemical characteristics, they can interact or even dissolve the coating and thus, come into contact with the metallic substrate. Finally, the coating design is important as well. It should be defect free and with good adhesion to the metallic substrate. Besides, it

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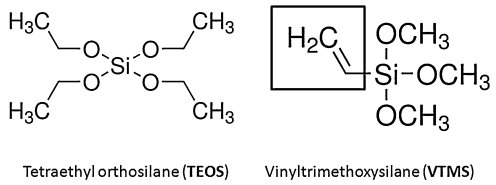

Fig. 1. Chemical structures of the inorganic (TEOS) and organic (VTMS) precursors for the hybrid sol–gel film. The organic group is enclosed in a box.

has to be adequately formulated, in order to avoid migration of chemicals into the food [10].

The present work addresses the electrochemical behavior of hybrid sol–gel films applied on a commercial tinplate immersed in two food-simulating solutions: 0.1 M NaCl solution, to reproduce seafood environment, and 0.1 M citric acid/sodium citrate buffer solution, commonly used to simulate fruit juices or pickled sauce. The initial step will be necessarily the characterization of bare tinplate in the same media.

2. Experimental design

2.1. Materials

The hybrid sol–gel solution was made from tetraethylorthosilane (TEOS) as the inorganic precursor sol and vinyltrimethoxysilane (VTMS) as the organic one. Fig. 1 displays the structures of TEOS and VTMS, the latter has three hydrolyzable groups (Si–OR) and an additional group (Si–R′) that provides certain flexibility to the film. This compound is included in the "materials and articles intended to come into in contact with food" (RD 866/2008) [19].

The procedure followed for preparing both sols was the same: 5 ml of the precursor were mixed with 5 ml of 2-propanol and 0.65 ml of HNO_3 (Baker, 70%) solution, pH = 0.5, in a 25 ml beaker under mechanical stirring for 60 min at room temperature. After mixing, the final solution was subjected to ultrasonic stirring for 60 min (power 130 W and frequency 20 kHz). The resulting sol–gel was aged during 9 days before deposition. This is the minimum ageing time necessary to obtain a uniform film.

The commercial tinplate samples (3 cm × 5 cm × 0.2 cm) were cleaned before the deposition using an ultrasonic bath in acetone, after, they were rinsed with soapy water and finally with distilled water. The hybrid sol–gel films were obtained by a dip-coating procedure at 180 mm/min withdrawal speed with a holding time of 120 s. The curing process was conducted at 155 °C during 20 min.

2.2. Experimental techniques

Several techniques were used to characterize the coated tinplate samples: Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) techniques. The equipment employed was an Electroscan JSM-54 model JEOL 5410 equipped with an energy dispersive X-ray detector Link ISIS 300, the acceleration voltage was 20 kV. X-ray diffraction patterns were collected using a Siemens D5000® powder diffractometer with monochromatized CuK_α radiation (λ = 1.54 Å) from $2\theta = 10^\circ$ up to $2\theta = 90^\circ$. The film thicknesses were evaluated by two dimensional mechanical profile acquisitions using a Dektak® 150 Surface Profiler (Veeco).

The electrochemical behavior were assessed by means of potentiodynamic polarization experiments, performed from −0.200 V with respect to the Open Circuit Potential (OCP) up to reaching current density values in the order of mA cm^{-2}, at 0.4 mV s^{-1} scan rate. The Electrochemical Impedance Spectroscopy (EIS) measurements were carried out in the frequency window from 100 kHz down to 10 mHz at 5 points per decade and 10 mV_{rms} sinusoidal perturbation. The measurements were carried out at the OCP.

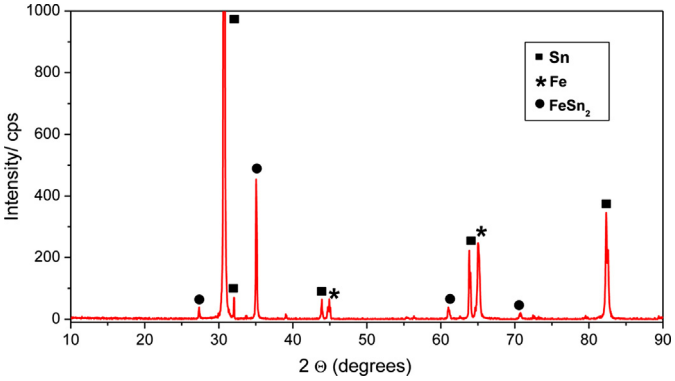

Fig. 2. X-ray diffractogram of tinplate samples, indicating the main crystalline compounds.

The electrochemical measurements were performed using in an AUTOLAB® 30 Potentiostat (from EcoChemie). All the measurements were conducted with a three-electrode arrangement at constant temperature (T = 23 °C) in aerated conditions: the working electrode was the tinplate sample with an exposed area of 1.3 cm^2; the reference and the counter-electrode were a saturated calomel electrode (SCE) and a large size graphite sheet, respectively. The electrolyte employed was a 0.1 M citric acid/sodium citrate buffer solution at pH = 4.3 or 0.1 M NaCl solution. In order to verify reproducibility of the results, at least two samples were tested per conditions.

3. Results and discussion

3.1. Bare tinplate

3.1.1. Surface characterization

Commercial tinplate specimens with a two-sided tin coating weight of 2.8 g m^{-2} were studied. The specimens had a "stone surface finishing", which is characterized by directional grindstone patterns and by a mild heat treatment after the tin electroplating to generate through diffusion the layer of intermetallic $FeSn_2$. This type of surface finishing is especially suitable to avoid scratches during the printing and can making processes.

Fig. 2 depicts the X-ray diffractogram obtained for tinplate samples. The presence of the $FeSn_2$ alloy is corroborated. On the other hand, the directional pattern is observed by the SEM secondary electron micrographs that are shown in Fig. 3a and b. The corresponding EDX spectra (see Fig. 3c) reveal a heterogeneous Sn distribution. Thus, the lighter bands are richer in Sn in comparison to the darker ones.

3.1.2. Electrochemical behavior of the bare tinplate

Fig. 4 shows the polarization curves of bare tinplate samples in the two tested media, the data were acquired after 40 min immersion, time required to stabilize the potential. The samples immersed in citric/citrate solution exhibit a plateau in the cathodic branch, indicative of limiting oxygen current. This can be due to a partial electrode blockage by the citrate ions adsorption [20,21]. The equilibrium potential at −0.69 V vs SCE, is associated with a Sn(II)-oxide/hydroxide layer [22]. The anodic branch shows high current densities values indicating an intense dissolution process. At −0.45 V vs SCE it can be observed an additional current minimum peak. Its interpretation is uncertain, some authors attribute it to the formation of Sn(IV) species [4,20,22]. Nevertheless, Chan [23] found white salts on the tin electrode after an anodic