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Structural characterization and barrier properties of hybrid sol-gel films applied on tinplate

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ABSTRACT

Several hybrid sol-gel formulations applied on tinplate were studied. The organic precursor was vinyltrimethoxysilane (VTMS) and the inorganic one was tetraethylorthosilane (TEOS). The characterization was performed by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and Fourier Transform Infrared Spectroscopy (FTIR). The optimization of the curing parameters was made by kinetics analysis based on Differential Scanning Calorimetry (DSC) measurements. The barrier properties were evaluated by Electrochemical Impedance Spectroscopy (EIS) technique.

The results indicated that only sol-gel solutions with high inorganic precursor ratios are able to form a continuous film, necessary to provide good barrier properties. Thus, tinplate coated with 25% VTMS and 75% TEOS formulation exhibited the better protection properties in the studied medium.

1. Introduction

Sol-gel process is a well-known technology that can be used to obtain inorganic as well as hybrid (organically modified inorganic) films. The obtained coatings provide good adhesion and corrosion protection to a wide range of metallic substrates [1]. The technique is based on the hydrolysis and condensation of metal alcoxides, **M-(OR)$_n$**. R represents an organic (typically alkyl) group and M denotes a metal or semi-metal (commonly silicon). Eqs. (1), (2a) and (2b) illustrate the involved reactions for an alkoxysilane [2]:

$$\text{Si–OR} + H_2O \rightarrow \text{Si–OH} + \text{ROH} \quad \textit{Hydrolysis} \tag{1}$$

$$\text{Si–OH} + \text{Si–OH} \rightarrow \text{Si–O–Si} + H_2O \quad \textit{Condensation} \tag{2a}$$

$$\text{Si–OH} + \text{Si–OR} \rightarrow \text{Si–O–Si} + \text{ROH} \quad \textit{Condensation} \tag{2b}$$

In Eq. (1), the Si–OR groups are hydrolyzed, generating reactive Si–OH, which undergo condensation reactions by elimination of water or alcohol (Eq. (2a) or (2b)). The result is a stepwise growth of the oxide network [3].

One advantage of this process is the possibility of designing tailored coatings using precursors of different nature. In this way, not only the chemical nature but also the morphology of the film, i.e., parameters like thickness, stiffness or porosity, can be controlled [4,5].

Traditionally, sol-gel technology employed inorganic precursors, M(OR)$_n$, where OR represent reactive (hydrolyzable) groups, thus, the result is an inorganic network which provides an stable bonding to the metallic or to the native oxide substrate. More recently, the use of organic precursors together with inorganic ones allows the introduction of certain functionality into the network, triggered by the non-hydrolyzable organic group (R′), bonded to the metal (M), **R′–M**, which is not involved in the network formation. The obtained hybrid films exhibit a wide range of properties, depending on the organic/inorganic ratio. Thus, the organic components provide flexibility, thickness and functionality to be compatible with paints. On the other side, the inorganic precursors improve the cross-linking density and the adhesion to the metallic substrate [2,6].

In the last decades, variety of hybrid sol-gel films were formulated to protect metallic substrates with noteworthy success, including aluminium alloys [2,7–9], carbon steel [10,11] or stainless steel [12,13]. The present work deals with the use of the hybrid sol-gel film applied on tinplate for food packaging industry. This system shows certain peculiarities that may justify the less exploitation of this technology. Thus, the commercial tinplate is a complex stratified system that essentially consists in tin electroplating on cold-rolled, low carbon steel; after that, it is submitted to a flow-melting process resulting a tin-iron alloy, $FeSn_2$, which protects the steel to aggressive species. The outer layer is made by chromium and tin oxides obtaining from a passivation treatment, that prevents tin oxide growth and sulfuration processes [14]. One important aspect to take into consideration is the chemical nature of the foodstuff that can corrode the can. The iron or tin species generated may contaminate the food, causing potential health problems [15,16]. In this context, the use of organic-inorganic coatings obtained by sol-

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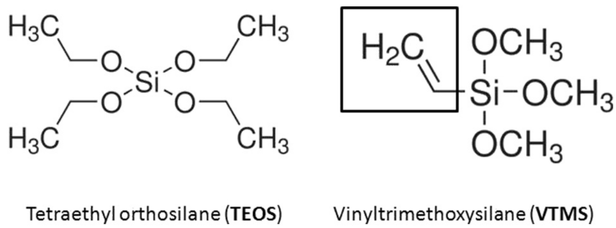

Fig. 1. Chemical structures of the inorganic (TEOS) and organic (VTMS) precursors employed for the hybrid sol-gel synthesis. The organic group is enclosed in a box.

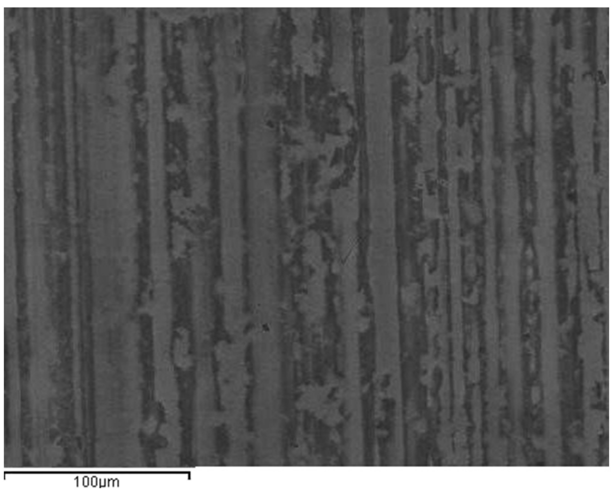

Fig. 2. SEI (Secondary Electron Image) of bare tinplate samples showing the banded structure, characteristic of the commercial stone finishing. The magnification is 350×.

gel technology stands for a new approach to the food can preservation [17–20]. Despite the advantages provided by these hybrid films, some critical aspects must be considered, in order to obtain defect free films and with good barrier properties, which avoid migration of chemicals into the food. They have to be adequately formulated, which means that the relative amounts of each type of precursors used to prepare the sol-gel coating must be the optimum to obtain a compact and, at the same time, flexible film [17,21]. In this line, the study of the cure kinetics is an important point to take into account. This allows the understanding of the film formation mechanism, and the definition of the optimum curing parameters (i.e. time and temperature), both may modify depending on the nature and relative quantities of the precursors [22,23].

The present work deals with the synthesis and characterization of hybrid sol-gel films applied on commercial tinplate. Vinyltrimethoxysilane (VTMS) was used as organic precursor and Tetraethylorthosilane (TEOS) as inorganic one. Several organic/inorganic ratios were assessed to attain uniform films, essential point for achieving good barrier properties. The kinetics study of the best VTMS: TEOS ratios were performed. The obtained results were the curing parameters used to obtain the hybrid films used to assess the barrier properties.

Fig. 1 displays the structure of TEOS and VTMS precursors, the latter has three hydrolyzable groups (Si—OR) and an additional non-hydrolyzable group (Si—R′), which affords certain flexibility to the film. This latter compound is included in the materials and articles intended to be exposed to foodstuff, according to the European Regulation (EU) No. 10/2011 [24].

2. Experimental design

2.1. Materials

The hybrid sol–gel solutions were made from tetraethyl-orthosilane (TEOS) as inorganic precursor and vinyltrimethoxysilane (VTMS) as the organic one. 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 at pH = 0.5, in a 25 mL beaker

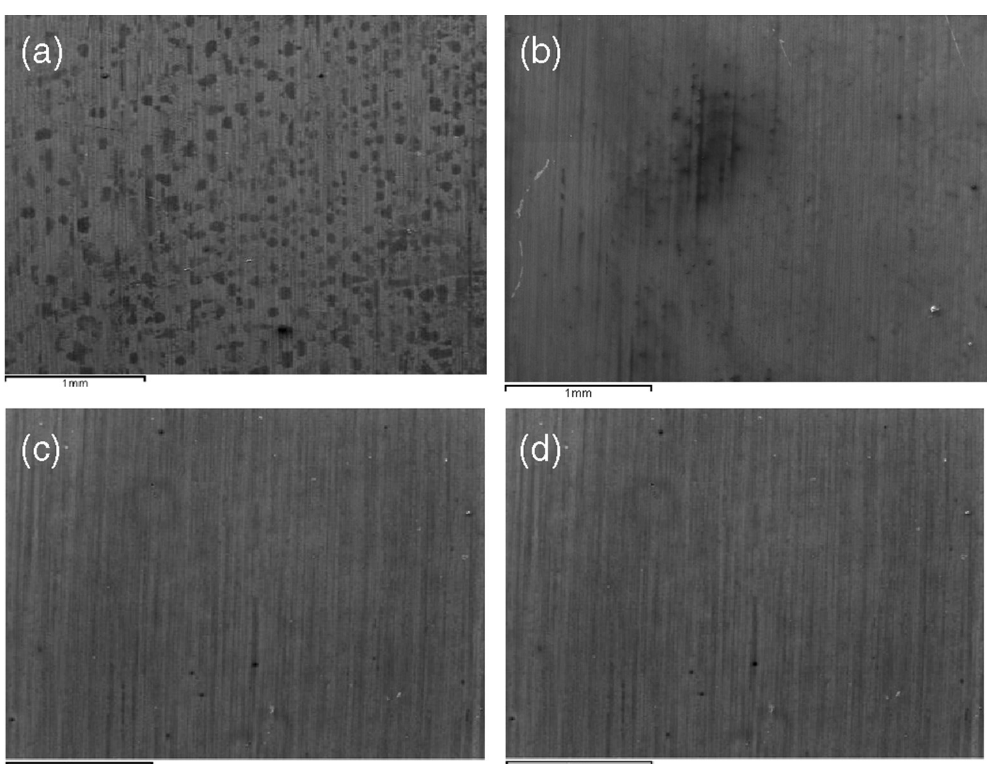

Fig. 3. SEI (Secondary Electron Image) of tinplate samples coated with the sol-gel formulations: (a) VT100, (b) VT75, (c) VT50 and (d) VT25. The magnification is 35× in all of them.