



## Steel protection using sol–gel coatings in simulated concrete pore solution contaminated with chloride



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### ABSTRACT

This work compares the anticorrosion features of polysiloxane hybrid films deposited on carbon steel substrates by dip-coating. To assess the influence of the components, sol–gel coatings were prepared from condensation and polymerization of TEOS and MPTS, TEOS and MTES, TMOS and MPTS or TMOS and MTES mixtures in three molar ratios. The corrosion protection of the coatings was evaluated by means of polarization curves and electrochemical impedance spectroscopy measurements. The coatings' thickness was quantified by field emission-scanning electron microscopy. The results indicate that all the coatings improved the corrosion resistance of carbon steel in an alkaline environment contaminated with 3 wt.%NaCl solution and show that the protective properties of the coating were especially improved when MTES was added to the formulations and when the TMOS/MPTS mixture was used, probably due to a highly cross-linked network and a greater coating thickness, capable of delaying the corrosion process.

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### 1. Introduction

Corrosion of reinforcing steel is one of the main causes of premature failure of reinforced concrete structures (RCS). Steel rebars embedded in concrete are protected from corrosion by a thin oxide layer that is formed and maintained on their surface thanks to the high pH level of the surrounding concrete [1–3]. Several ions, produced by hydration of the cement paste, dissolve in the pore water to form an aqueous solution of nearly pH 12.5. This provides passivity to the reinforcing bars. However, if chloride ions are present above a certain threshold value in the concrete, especially near the rebar surface, they can depassivate the steel [4,5].

The corrosion of carbon steel rebars damages RCS in two ways. Firstly it reduces the cross-section area of the steel bars, and secondly it produces corrosion products of a larger volume than the steel itself, giving rise to tensile stresses in the concrete that result in cracking and eventual structural failure [1,6–8].

An idea of the financial impact of RCS corrosion can be seen in the fact that costs attributed to this phenomenon in Spain were of the order of  $1.2 \times 10^9$  euro in 1995 [9], and it is currently estimated that 3–4% of the gross national product (GNP) in developed countries is directly or indirectly connected to RCS maintenance and repair operations [10].

Corrosion protection of RCS is often achieved by adding corrosion inhibitors to the concrete, using high performance concrete mixtures,

protective coatings or stainless steel (SS) rebars, or applying cathodic protection (CP) systems. Among these methods, the use of protective coatings is one of the most economical and effective methods since it can establish a physical barrier between aggressive ions and the steel rebars.

Different types of protective coatings have been developed, both organic (paint) and inorganic (ceramic), as well as combinations of the two. However, coatings based on polymeric materials have low thermal stability and poor adhesion to the metal surface, and inorganic coatings suffer limitations due to micro cracks, porosity and high internal stress leading to adhesion failures and thickness limitations [11]. Alternative research on organic–inorganic hybrid materials deposited by sol–gel dip or spin-coating on various substrates, mostly metals, has intensified in recent years due to their excellent anticorrosion properties [11–18].

Much of the initial work concerning corrosion protection offered by sol–gel coatings was conducted using Class I hybrids, in which the inorganic and organic components are bonded by van der Waals forces [12, 19,20]. For instance, dispersing poly(methyl methacrylate) (PMMA) into zirconia ( $ZrO_2$ ) creates a layer that improves the corrosion resistance of SS [19]. However, phase separation of the coating layer and delamination can cause its long-term failure. The degradation of coating properties caused by phase separation can be reduced using Class II hybrids, in which the organic and inorganic phases are linked by covalent bonds [21,22]. A large number of Class II hybrid materials are formed by the hydrolytic condensation of an alkoxy silane ( $RSi(OR')_3$ ) precursor modified with a polymerizable R group, such as epoxy, methacrylic or acrylic organofunctional species. Among the various available organic substituted trialkoxysilanes, 3-methacryloxy-propyl-trimethoxysilane

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(MPTS) is one of the potential starting materials for the preparation of this type of tetraalkoxysilane hybrids such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS). Due to their cross-linked structure, Class II hybrid coatings are not subject to phase separation or delamination like Class I hybrids [23].

The aim of this paper is to study using electrochemical techniques the protective properties of polysiloxane hybrid coatings deposited on carbon steel substrates by dip-coating and immersed in an alkaline saturated calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) solution, in exposure to a simulated concrete pore (SCP) solution contaminated with 3 wt.% NaCl.

## 2. Experimental

The reagents used were: 3-methacryloxy-propyl-trimethoxysilane ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$  (MPTS), from Sigma-Aldrich), methyl-triethoxysilane ( $(\text{CH}_3)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$  (MTES), from Sigma-Aldrich), tetraethyl orthosilicate ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$  (TEOS), from Sigma-Aldrich), tetramethyl orthosilicate ( $\text{Si}(\text{OCH}_3)_4$  (TMOS), from Sigma-Aldrich) and benzoyl peroxide (BPO), from VWR International Eurolab). All reagents were of laboratory grade.

Sol-gel coatings were prepared by condensation and polymerization of the TEOS/MPTS, TEOS/MTES, TMOS/MPTS or TMOS/MTES mixtures. Sol-gel reactions were achieved by mixing 5 g of MPTS or MTES with the TEOS or TMOS amounts required to obtain the three molar ratios: 0.5 (R0.5), 1 (R1), and 2 (R2). Afterwards,  $\text{HNO}_3$ -acidified water (pH 1, and molar ratio  $\text{H}_2\text{O}/\text{Si} = 3.5$ ) was added, using ethanol as solvent (molar ratio ethanol/ $\text{H}_2\text{O} = 1.0$ ). At the same time, the desired amounts of the thermal initiator of polymerization (BPO) were added to the mixtures (molar ratio BPO/MPTS or BPO/MTES = 0.01).

The organic-inorganic hybrid coatings were deposited by dip coating onto carbon steel substrates measuring  $52 \times 30 \times 1 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness), having the chemical composition (wt.%) 0.078 C, <0.030 Si, 0.27 Mn, 0.016 P, 0.033 S, 0.016 Cr, 0.013 Ni, <0.010 Mo, 0.026 Al, 0.029 Cu, and balance Fe. The specimens were polished with grade 600 silicon carbide paper and finally washed with double distilled water and degreased with acetone to obtain a reproducible surface finish. The carbon steel was then dipped in the solution, withdrawn at a rate of  $14 \text{ mm min}^{-1}$ , and air-dried for approximately 10 min. This procedure was carried out twice, after which the coated steels were heated at  $65^\circ\text{C}$  for 24 h and cured at  $160^\circ\text{C}$  for 3 h.

The thickness of the coatings was determined by field emission-scanning electron microscopy using a FE-SEM FEI Nova NanoSEM 230 equipped with an EDAX Genesis XM2i analyzer.

The corrosion behavior of coated and uncoated carbon steel specimens was evaluated by means of polarization curves and electrochemical impedance spectroscopy (EIS) measurements. Polarization curves were recorded on the carbon steel specimens after 2 and 48 h of immersion in a saturated  $\text{Ca}(\text{OH})_2$  solution at pH 12–13 (chemical analysis quality from Merck) containing 3 wt.% NaCl (99% pure from Panreac PRS-CODEX), and EIS was performed after 2, 7, 15 and 30 days of experimentation in an identical test solution. An active surface area of steel of  $0.64 \text{ cm}^2$  was exposed to the test solution.

A PARC 273A Potentiostat (EG&G Instruments) and a Solartron 1250 Frequency Response Analyzer were utilized for polarization curves and EIS measurements. The pitting potential ( $E_p$ ) was evaluated from polarization curves at a scan rate of  $0.1667 \text{ mV s}^{-1}$  [24].  $E_p$  was defined as the potential value at which the corrosion current density ( $i_{\text{corr}}$ ) rises sharply. The EIS technique is a non-destructive technique that can provide information on coating properties and steel corrosion over time. EIS measurements were recorded at the corrosion potential ( $E_{\text{corr}}$ ) in a frequency range from 64 kHz to 10 mHz with a logarithmic sweeping frequency of 5 points per decade. EIS involved the imposition of a 10 mV rms amplitude excitation voltage.

The Avesta-type cell was used in a three-electrode configuration with the sample as the working electrode, a saturated calomel electrode (SCE) as reference, and a platinum mesh as counter electrode. All the

experiments were performed at room temperature at least three times to confirm the reproducibility of the results.

## 3. Results and discussion

Fig. 1 shows the polarization curves for uncoated and coated steel with polysiloxane hybrids synthesized from the TEOS/MPTS, TEOS/MTES, TMOS/MPTS, and TMOS/MTES mixtures, using R0.5, R1 and R2 molar ratios, recorded after 2 and 48 h of immersion in a saturated  $\text{Ca}(\text{OH})_2$  solution (pH 12.5) contaminated with 3 wt.% NaCl.

The shape of the polarization curves indicates that all the coated steel exhibited stable passive behavior in the  $\text{Ca}(\text{OH})_2$  solution. In Fig. 1, for all the tested coated steels, no pitting potential was observed, indicating the excellent anticorrosion properties of the coatings. Only a rapid increase in the anodic current density ( $i_{\text{corr}}$ ) at  $\sim 700$  or  $800 \text{ mV}$  vs. SCE potential was observed, which may be due to the oxidation of hydroxyl ions ( $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ ).

Table 1 sets out the  $E_{\text{corr}}$  values for 2 and 48 h of immersion in a saturated  $\text{Ca}(\text{OH})_2$  solution containing 3 wt.% NaCl. The  $E_{\text{corr}}$  values for coated steel were close to the values obtained for uncoated steel irrespective of the experimentation time. For uncoated steel the  $E_{\text{corr}}$  was  $-0.45$  and  $-0.38 \text{ V}$  vs. SCE for 2 and 48 h immersion, respectively, while the  $E_{\text{corr}}$  values for coated steel were in the range from  $-0.22 \text{ V}$  to  $-0.46 \text{ V}$  vs. SCE. Therefore, the nature of the reagents and the molar ratio used in the synthesis of polysiloxane hybrid coatings for carbon steel do not seem to have a clear influence on the  $E_{\text{corr}}$  value.

Table 1 also shows the  $i_{\text{corr}}$  values for 2 and 48 h of immersion in a saturated  $\text{Ca}(\text{OH})_2$  solution containing 3 wt.% NaCl. The uncoated steel plate presented active behavior, with an  $i_{\text{corr}}$  between 30 and  $19 \mu\text{A cm}^{-2}$ , suggesting that the oxide film growing on the metal surface was not protective and that chloride ions attacked the passive layer, causing its breakdown. For coated steel, the application of the sol-gel coatings improved the corrosion behavior of the samples, and after 2 h of immersion (see Fig. 1) the  $i_{\text{corr}}$  was 1–2 orders of magnitude lower than for uncoated steel, with  $i_{\text{corr}}$  values between 7.6 and  $0.3 \mu\text{A cm}^{-2}$ . For 48 h of immersion, most of the coated steels showed  $i_{\text{corr}}$  values higher, indicating lower long-term resistance to chloride ion penetration. However, their  $i_{\text{corr}}$  values were always lower than that obtained for uncoated steel. The coatings afforded corrosion protection to the substrate, which was probably due to the quite well covered surface of the steel which prevented the aggressive ions from coming into contact with the metal surface, thus retarding the corrosion process. Fig. 2 shows two SEM images of the surface of the coatings synthesized from the (a) TMOS/MPTS and (b) TEOS/MPTS mixtures with the molar ratio of 0.5 adhered to the steel before the corrosion tests. The micrograph of the film synthesized from the TMOS/MPTS mixture showed a surface enough homogeneous with some small particles deposited in it, probably associated with sample handling. All the other films had a similar morphology, except for the coating obtained from the TEOS/MPTS mixture that presented a surface with several defects and also some irregularities, presenting the highest  $i_{\text{corr}}$  values.

Determination of the porosity of the coatings is difficult because of the small size of the pores. However, assuming that the coatings are electrochemically inert at low overpotentials, coating porosity can be estimated from the polarization curves using the empirical relation [25–27]:

$$F = \left( R_{p,m} / R_p \right) \times 10^{-\left| \frac{\Delta E_{\text{corr}}}{\beta_a} \right|} \quad (1)$$

where  $F$  is the total coating porosity,  $R_{p,m}$  is the polarization resistance of the base material,  $R_p$  is the measured polarization resistance of the coated steel,  $\Delta E_{\text{corr}}$  is the difference between the corrosion potentials (coating and substrate), and  $\beta_a$  is the anodic Tafel slope of the base material. The coating porosity is closely related to coating quality and

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