



Study of the degradation of hybrid sol–gel coatings in aqueous medium



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ABSTRACT

The design and development of suitable multilayered functional coatings for delaying corrosion advance in metals and become controlled-release vehicles requires that the properties of the coatings are known. Coatings prepared by the sol–gel method provide a good approach as protective layers on metallic surfaces. This kind of coating can be prepared from pure chemical reagents at room temperature and atmospheric pressure, with compositions in a very wide range of environmentally non-aggressive precursors. Sol–gel coatings based on siloxane bonded units were prepared, starting with an organic–inorganic hybrid system. Synthesis procedures included acid-catalysed hydrolysis, sol preparation, and the subsequent gelation and drying. The alkoxide precursors used were methyl-triethoxysilane (MTMOS) and tetraethyl-orthosilicate (TEOS) in molar ratios of 10:0, 9:1, 8:2 and 7:3. After determination of the optimal synthesis parameters, the materials were characterised by solid ²⁹Si nuclear magnetic resonance (²⁹Si NMR), Fourier transform infrared spectroscopy (FTIR), contact angle measurement and electrochemical impedance spectroscopy (EIS) test. Finally, the materials were assayed by controlling their weight in contact with water, to determine their ability to degrade by hydrolysis. Electrochemical analysis reveals the formation of pores and water uptake during the degradation. The quantity of TEOS is one of the principal parameters that determine the kinetics of degradation. There is a correlation between the degradation process obtained for long periods and the electrochemical parameters obtained by EIS in short times. The study tries to incorporate knowledge that can be used for designing the degradation process of the functional coatings and to control their properties in short times.

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1. Introduction

The use of *sol–gel* coatings as replacements for chromate conversion coatings in the pre-treatment for different metallic alloys has become widespread in the past decades. *Sol–gel* coatings have several advantages, e.g., they are an environmentally friendly technology. Another important feature is the good adherence obtained between the metallic surface and the *sol–gel* film, which is based on the establishment of chemical bonding (M–O–M) from the condensation reactions between metal hydroxyls (M–OH) and alkoxide hydrolysable groups (commonly Si–OH) [1].

Additionally, these *sol–gel* materials are biodegradable and biodegradable leaching non-toxic degradation products [2]. Since *sol–gel* technology uses a relative low temperature during formation of

the inorganic matrix, various organic, inorganic and biological molecules can be introduced as dopant agents with no degradation risk. For these reasons, *sol–gel* materials have been extensively used as controlled-release matrices [2–5].

Using *sol–gel* technology, organic–inorganic hybrid materials can be prepared by a silane precursor containing an organic group. Thus, silica gel obtained by the *sol–gel* technology is an inorganic or hybrid (organic–inorganic) polymer produced synthetically by the controlled hydrolysis and condensation of alkoxy silanes. The synthesis of *sol–gel* silica occurs from liquid precursors *sol* via the initial formation of *wet gels*, in which the inorganic network is surrounded by solvent, which are later removed to yield a dry material. Depending on the organic group present in the alkoxy silane, the hybrid character of the final material will be defined. In contrast to common glass, which is a viscous fluid obtained by the high temperature fusion of SiO₂, *sol–gel* silica is an amorphous, porous material, which is synthesised in mild conditions [6,7].

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The use of organofunctional silanes as precursors leads to the formation of an organically modified hybrid that improves the flexibility and density of the films and, additionally, gives functionality to the coating so that it is compatible with the subsequent paint system [8–11]. Nevertheless, the characteristic porosity exhibited by these films leads to worse anticorrosive properties, mainly in the long term [12–15]. However, these materials have several attractive features when compared to inorganic sol–gel (e.g. hydrophobicity and durability) [5] and provide a versatile way to prepare modified sol–gel coatings that can be easily applied to implant surfaces.

Finally, the influence of the initial alkoxy silanes selected (the composition of the precursors) in the degradation of the material has not yet been studied in depth. Aspects such as the type of alkoxy silane used or the organic content in the final silicon network can define the material capacity to degrade [8]. Depending on the degradation kinetics the design of the coating system will need to be done by the incorporation of layers able to reduce the permeability to the electrolyte.

The present study reports the synthesis via sol–gel method of hybrid (silica and organic chains) networks with a mixture of two alkoxy silanes MTMOS and TEOS, which can be used as functional coatings. MTMOS alkoxy silane provides an organic character (a methyl group) to the network, while TEOS increases crosslinking kinetics [16]. Different molar proportions MTMOS:TEOS were used. The aim of the work is to investigate how changes in the %TEOS in the hybrid network influence on the degradation of the matrix. In order to characterise the network formation, a spectroscopic study was performed by FTIR and RMN. Moreover, EIS technique was used to study the initial pore structure of the materials and further changes in the coating because of degradation, fundamentally assessing its capacity to resist pore formation and water uptake, recording both parameters as a function of time. Finally, the results of the weight loss in contact with water are reported and correlated with the physicochemical properties of the different networks.

2. Experimental

2.1. Materials

2.1.1. Sol–gel synthesis

Organic–inorganic hybrid coatings were synthesised from MTMOS (Sigma–Aldrich) and TEOS (Sigma–Aldrich). Coatings with different MTMOS:TEOS molar ratios were prepared 10:0 (10M:0T); 9:1 (9M:1T); 8:2 (8M:2T); 7:3 (7M:3T). To ensure a miscible solution of the silane precursors, 2-propanol (Sigma–Aldrich) was used as a co-solvent, in a volume ratio of alcohol:precursor 1:1. A stoichiometric amount of water acidified with HNO₃ (pH = 1), was added as the catalyst of the reaction. After the addition of the catalyst, solutions were stirred for 1 h and set for another hour at room temperature before their deposition on a substrate. This period of time (2 h) is necessary to ensure the maximum extent of the hydrolysis of the methoxy groups of MTMOS and the ethoxy of TEOS.

2.1.2. Sol–gel coatings

Two types of samples were obtained in order to characterise the coatings: those deposited on a metal substrate and those without a substrate, a free film material.

Stainless steel AISI 316-L plates (5 cm × 5 cm, RNSinox, S.L.) were used as a substrate for sol–gel deposition. The plates were cleaned with acetone to remove impurities and oil. A dipping device (KSV instrument-KSV DC) with a controlled withdrawal speed was used for the film deposition. Plates were immersed into the dissolution at a speed of 100 cm min⁻¹, left for 1 min and the plates were then removed at the same speed.

Table 1

Thermal treatment applied to obtain the final material.

Material	MTMOS	TEOS	MTMOS:TEOS
Cure temperature (°C)	100	50	80
Cure time (min)	120	120	120

In order to obtain a free sol–gel film, Teflon moulds were used. 3 ml of sol were poured into the mould to obtain a homogeneous final film.

The coatings were dried and cured using the thermal process described in Table 1. Curing conditions were previously established by means of the NMR spectroscopy, to ensure the maximum cross-linking, and SEM to prove that the film obtained was homogeneous and free of cracks [5]. During the thermal treatment, the condensation of the remaining OH groups was promoted and evaporation of the solvents occurred, resulting in the final network.

2.1.3. Chemical characterisation

²⁹Si NMR solid spectroscopy was used to determine the Si–O–Si cross-linking density after curing treatment. For the analysis of samples, the obtained free films were ground into powder. Spectra were recorded on a Bruker 400 AVANCE II WB PLUS spectrometer, equipped with a CP-MAS (cross polarisation magic angle spinning) probe. The powder samples were placed in a rotor sample tube of 4 mm. The sample spinning speed was 7.0 kHz. The pulse sequence used was the Bruker standard, frequency was 79.5 MHz, spectral width was 55 kHz, contact time was 2 ms and delay time was 5 s.

The structure of the hybrid coatings was examined by Fourier-transform infrared (FT-IR) spectroscopy (Model FTIR 6700, NICOLET). Free films of each precursor and the mixtures were prepared. The spectra were recorded on the attenuated total reflectance (ATR) mode and the wavelength range was between 4000 and 400 cm⁻¹.

2.2. Contact angle measurement

The wettability of the coatings was determined by the measurement of the contact angle of deionised water onto the sol–gel surface using an automatic contact angle meter (DATAPHYSICS OCA 20 Goniometer). The sol–gel coatings were deposited onto stainless steel plates and a sessile drop of 10 μl deionised water was placed on the coating surface. The wettability was determined by the half angle method. The value given is the mean value of at least 11 measurements. For the calculation of contact angle values, a statistical analysis was performed. Mean and standard deviation values were calculated using the one-way ANOVA statistical technique. The error protection method used in this research was the Tukey HSD method and the confidence limit used was 95%.

2.3. Hydrolysis degradation test

The hydrolysis degradation test was performed by soaking the coatings in distilled water at 37 °C, during 9 weeks. The hydrolytic degradation was evaluated by weight loss of the coatings before and after soaking in distilled water during different periods of time. After soaking, the samples were dried in an oven at 37 °C for 24 h and they were weighed. Each data point is the average of three individual measurements.

2.4. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy tests were carried out on coated samples deposited on a metallic substrate exposed to 3.5% NaCl (by weight) in deionised water for up to 24 h. A three

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