



Effect of Na-Montmorillonite sonication on the protective properties of hybrid silica coatings



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ABSTRACT

This work deals with the effect of the sonication treatment applied to an aqueous suspension of sodium montmorillonite nanoparticles used to prepare hybrid clay-organosilane derived sol-gel films. The sol-gel films were obtained from a mixture of 3-glycidoxypropyltrimethoxysilane (GPTMS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) adding 2 wt% of sodium montmorillonite suspension after sonication. The sol-gel layers were applied onto hot dip galvanized (HDG) steel plates. The influence of the duration of the sonication treatment (i.e. 0, 1, 3 and 12 hours) on both the structure as well as on the electrochemical properties of the sol-gel films was analyzed in details. The effect of different sonication times on the structure of the sol-gel film was investigated by means of solid state Nuclear Magnetic Resonance (NMR), X-Ray diffraction (XRD) and Infra-Red (FT-IR) spectroscopy. The corrosion protection properties of the different sol-gel layers were investigated mainly by means of electrochemical techniques. The structural characterization (NMR, XRD, FT-IR) of the coating proved that interactions between the montmorillonite plates and the silica-based sol-gel network take place, with changing the local environment of Al sites in the clay. The potentiodynamic measurements as well as the EIS confirmed the beneficial effects of the presence of the Na-MMT and of the sonication treatment.

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1. Introduction

It is widely known that due to their efficient properties as coupling agents, organosilane molecules represent an interesting and environmentally friendly alternative in the field of surface conversion treatments [1–12]. It is recognized that these materials act as adhesion promoters between a metal substrate and an organic coating, thus improving the service life of the complete protection system. In particular, the effective use of hybrid sol-gel films applied onto hot dip galvanized steel (HDG) to increase the adhesion between a metallic substrate and an organic coating is reported in literature [13–15]. In addition, literature reports also that the corrosion protection properties conferred to the metallic substrate by these hybrid layers themselves is noteworthy [16]. In fact, these materials are able to behave as a physical barrier against water and aggressive ion diffusion to the substrate [17] thus decreasing the corrosion reaction rate on the metal surface. For this reason, to further improve the corrosion protection properties of these hybrid layers suitable nanoparticles were incorporated inside the hybrid matrix [18–23]. Among the different particles which can be

exploited to improve the properties of the sol-gel films, the beneficial effect of the presence of about 1–2wt% of nano-clay (sodium montmorillonite, Na-MMT) in the hybrid matrix was evidenced in a previous study [24]. According to previous results [25,26], it was found that the properties of the sol-gel films were strongly dependent on granulometric distribution, exfoliation state, dispersion and concentration of clays in the studied matrix. Moreover the effect of an ultrasonic treatment on the rheological properties of different water-based organosilane–nanoclay solutions and on the final corrosion protection properties of the cured hybrid films was investigated [27].

In this paper the effect of the duration of a sonication treatment on the properties of organosilanes derived sol-gel films containing clay nanoparticles was investigated. For this purpose, hot dip galvanized (HDG) steel plates were used as the substrate to coat. In particular, the influence of the duration of the sonication treatment on both the structure as well as on the electrochemical properties of the sol-gel films was analyzed in details. For this purpose, HDG steel samples were dipped into the hydrolysed organosilane solution, prepared from 3-glycidoxypropyltrimethoxysilane (GPTMS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) with 2wt% of sodium montmorillonite. The effect of different sonication times (i.e. 0, 1, 3 and 12 hours) on the structure of the sol-gel film was investigated by means of solid state Nuclear

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Table 1
Description of the investigated samples.

Name	Description	
	Amount of Na-MMT particles	Duration of the ultra-sonication
Neat Silane	-	-
0h_Sonication	2wt%	-
1h_Sonication	2wt%	1 hour
3h_Sonication	2wt%	3 hours
12h_Sonication	2wt%	12 hours

Magnetic Resonance (NMR), X-Ray diffraction (XRD) and infrared (FT-IR) spectroscopy. The corrosion protection properties of the different sol-gel layers were investigated mainly by means of electrochemical techniques such as potentiodynamic curves and electrochemical impedance spectroscopy (EIS). The test evidenced that the presence of the Na-MMT nanoparticles and the time of sonication strongly affect the structure of the sol-gel coating and its electrochemical impedance response.

2. Experimental

2.1. Materials

The organosilane precursors were 3-Glycidoxypropyltrimethoxysilane (GPTMS, Sigma–Aldrich, 99% purity), Tetraethoxysilane (TEOS, VWR, 98% purity) and Methyltriethoxysilane (MTES, VWR, 98% purity). These products were used as received without further purification.

The metallic substrates (supplied by ArcelorMittal, Belgium) consisted in continuous hot-dip galvanized steel sheets (0.15wt% Al). 60 mm × 80 mm plates were cut from the galvanized sheets and were used as substrate to coat. The samples were degreased with acetone before chemical etching. The chemical etching was performed by dipping for about 60 s the samples in a 10 wt% KOH solution maintained at 60° C.

The neat clay mineral used as filler was a sodium montmorillonite (Na-MMT, supplied by Southern Clay Products, USA), also called cloisite Na. The Na-MMT nanoparticles were ultrasonically dispersed in an aqueous solution. The ultrasonic treatment was performed during various times in a 50 ml beaker using a Hielscher UP100H sonicator with the power set to 13.5 W and controlled in temperature by using tap water circulation. According to a previous study [24] a two hours long sonication treatment was proved to ensure a complete exfoliation of the montmorillonite plates. To better investigate the effect of sonication, the treatment was applied to NaMMT solutions for different sonication times: 0 h, 1 h, 3 h and 12 h of continuous treatment. After the sonication treatment the pH of the dispersions was adjusted to 3.5 by adding hydrochloric acid. The aqueous suspension containing 2 wt% of Na-MMT, sonicated for different time intervals, was then added to the silane mixture (10 wt%), prepared with TEOS/GPTMS/MTES = 1/1/1 weight ratio.

The etched galvanized steel samples were rinsed in tap water and then in de-ionised water, and were dipped for 3 min in the different silane solutions. The withdraw rate was fixed at 0.2 m min⁻¹. The wet films were cured in oven for 20 minutes at 150 °C. Table 1 summarizes the investigated samples and highlights the labels used throughout the paper. To perform the chemical analyses the silane solutions were coated onto a Teflon sheet using a tape caster and cured in oven at 150 °C for 20 minutes. The cured films were peeled from the sheet and milled to obtain a fine powder which was used for infra-red (FT-IR), X-ray diffraction (XRD) and solid state nuclear magnetic resonance (NMR) analyses. A coating onto a Teflon sheet was also obtained from a TEOS/GPTMS/MTES solution, hydrolysed

under the same conditions but without clay addition. After curing and peeling from the substrate, the sample labeled “Neat silane” was used for comparison.

2.2. Techniques

The FT-IR spectra were recorded on a Thermo Optics Avatar 330 instrument, in transmission mode in the range 4000 - 400 cm⁻¹ using KBr pellets (64 scans, 4 cm⁻¹ resolution).

The X-ray diffraction (XRD) spectra were collected with a Rigaku D-Max III diffractometer using Cu K α radiation and a graphite monochromator in the diffracted beam. The XRD spectra of MMT and composite xerogels were collected in θ - 2θ configuration in the 1.0 - 80° (2θ) range with 0.05° sampling interval and 5 s counting time.

The solid state NMR analyses were carried out on a Bruker 700SB instrument working at a proton frequency of 700.23 MHz. ²⁷Al MAS spectra were recorded at 182.39 MHz, with $\pi/2$ Hahn-echo pulse length of 1.45 μ s, 1 s recycle delay, with acquisition of 4k scans. Samples were packed in a 3.2 mm zirconia rotor, which was spun at 20 kHz. Al(NO₃)_{3(aq)} was used as external secondary references. Electrochemical impedance spectroscopy measurements were carried out on the sol-gel coated galvanized steel samples to evaluate the effect of the different sonication time on the corrosion protection properties. The impedance spectra were obtained using a Parstat 2273 (Ametek). A conventional three-electrode cell was used. The working electrode was the investigated sample. A platinum ring and a Ag/AgCl (+205 mV vs. SHE) electrode were used as counter and reference electrode, respectively. A Faraday cage was used to minimize external interference on the system. The electrolytic solution was NaCl 0.1 M and the immersed area was about 1.5 cm². The impedance measurements were performed over frequencies ranging from 100 kHz to 10 mHz using an amplitude signal voltage of 10 mV. The EIS data were fitted using Zsimpwin® software. Using the same equipment and experimental set-up, potentiodynamic measurements were performed. Anodic and cathodic branches of the curves were separately collected starting from the open circuit potential. A scan rate of 0.166 mV/s was used. All the electrochemical measurements were duplicated to corroborate the experimental results.

3. Results

The structure of Na-MMT has been characterized with different techniques in order to detect possible structural changes as a consequence of addition to the silane mixture and sonication. The Na-MMT powder was characterized as received, without further treatments.

In the FT-IR spectrum (Fig. 1) of Na-MMT, the broad signal at 3446 cm⁻¹ is due to the OH stretching vibrations of adsorbed water, which shows the corresponding OH bending at 1630 cm⁻¹.

The signal at 3625 cm⁻¹ can be attributed to hydrogen bonded OH groups in the aluminosilicate lattice characterized by a high content of six-fold coordinated aluminum atoms (octahedral) [28]. The large band in the range 1250–950 cm⁻¹ clearly shows one main signal at 1040 cm⁻¹ and a shoulder at 1115 cm⁻¹, and represents the typical Si-O vibrational pattern of montmorillonites [29]. In the literature [30] it is reported that the band envelope in the range 1250–950 cm⁻¹ can be deconvoluted in four signals, one arising from the asymmetric stretching vibrations of apical Si-O bonds (bridging oxygen atoms between tetrahedral and octahedral sheets) and the remaining three bands due to Si-O stretching vibrations within the tetrahedral sheets. Position and intensities of these signals are strongly dependent on the substituting cation. The weak band at 915 cm⁻¹ is attributed to (Al₂OH) bending vibration

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