



Research paper

Filler-matrix interaction in sodium montmorillonite-organosilica nanocomposite coatings for corrosion protection



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ABSTRACT

Sodium montmorillonite/organosilica sol-gel coatings were obtained from a hydrolysed solution of 3-glycidopropyltrimethoxysilane (GPTMS), methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) with 2 wt% of sonicated sodium montmorillonite (Mt). The effect of different sonication times (0, 1, 3, 12 h) on the structure of both Mt and sol-gel clay-organosilica nanocomposites was investigated by means of ²⁹Si and ²⁷Al solid state nuclear magnetic resonance (NMR) and X-ray diffraction (XRD). Mt underwent relevant structural changes with the sonication treatment and the effect appeared time-dependent, although not linear. The structural changes induced on clay by the sonication process were kept in the clay-organosilica nanocomposite, according to ²⁹Si NMR. Mt addition to the hybrid sol-gel network led to decreasing the amount of completely condensed silicon units by formation of new Si-O-Al hetero-metallic bonds, as shown by ²⁷Al NMR results. Moreover, organosilica matrix and Mt appeared to interact even in the absence of the sonication treatment of the filler. The NMR study of GPTMS/MTES/Mt and TEOS/Mt samples clearly proves the interaction of Mt with the silsesquioxane (T) species in the obtained composites.

1. Introduction

Organosilane-derived sol-gel coatings have been widely studied in the field of metallic surface conversion treatment due to their capability to act as coupling agents between inorganic and organic materials, and, at the same time, to provide the substrate with improved corrosion resistance (Palanivel et al., 2003, 2005; van Ooij et al., 2005; Wang and Akid, 2007). Since comprehensive and interesting reviews on this topic are available in literature (Sathyanarayana and Yaseen, 1995; Wang and Bierwagen, 2009; Figueira et al., 2015), in this context it is deemed sufficient to recall that, even if organosilane sol-gel films are believed not to provide any active inhibition of the disruptive electrochemical process taking place on a metal exposed to an aggressive environment, these coatings ensure an effective barrier against water and aggressive species. As anodic and cathodic processes are activated and promoted by the presence of negatively charged ions and reducible species (oxygen, hydrogen, water), respectively, a decrease of their diffusion rate to the metal interface implies a slowdown of the overall corrosion rate.

In a previous work (Fedel et al., 2014), the effect on the electrochemical properties of the duration of a sonication treatment of organosilane-derived films containing clay nanoparticles was investigated.

The preliminary structural investigation of hybrid films applied on hot dip galvanized steel was also performed by means of solid state nuclear magnetic resonance (NMR) and Fourier transform infra-red (FT-IR) spectroscopy. This study exploited previous findings (Deflorian et al., 2010; Olivier et al., 2011; Motte et al., 2012; Poelman et al., 2015) concerning the effect of an ultrasonic treatment on the rheological properties of different water-based organosilane–nanoclay solutions and on the final corrosion protection properties. The reasons for investigating clay-organosilica nanocomposites (CON) rely on the need to improve the corrosion protection properties of the neat sol-gel film itself, by improving the barrier properties against water and aggressive ions permeation. Clay nanoparticles have been recognized to efficiently increase the barrier properties of polymeric coatings used for corrosion protection purposes (Malucelli et al., 2009; Huttunen-Saarivirta et al., 2013; Tomic et al., 2014). As far as sol-gel coatings are concerned, it was demonstrated (Fedel et al., 2015) that about 1–2 wt% of nano-clay (sodium montmorillonite) in the hybrid matrix led to a strong increase in barrier properties. However, critical parameters such as granulometric distribution, exfoliation state, concentration and dispersion of clays in the matrix require to be carefully controlled (Hang et al., 2007; Truc et al., 2008) since they affect CON interface features that, at their turn, influence the functional behavior.

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Literature reports various spectroscopic studies on both natural and synthetic montmorillonite aimed to clarify the clay structure, the distribution of cations such as Mg and Na (Weiss et al., 1987; Cuadros et al., 1999; Lausen et al., 1999; Viani et al., 2002; Alba et al., 2005; Cadars et al., 2011, 2012) and the effect of intercalation of water, ions, organic or silylated chains with different length (Dubbin and Boon Goh, 1997; Grandjean et al., 2003; Gougeon et al., 2006; McAlpine et al., 2006; Wen et al., 2006; Silva et al., 2011; Eisazadeh et al., 2012). FT-IR (Hrachova et al., 2009), XRD (Wen et al., 2006; Mishra et al., 2012) and multinuclear solid state NMR (Ocelli et al., 2000; Cadars et al., 2012), combined with TG analyses (Drachman et al., 1997) have been widely used to this purpose. The structural elucidation and the study on the intercalation effects by NMR were often performed on synthetic Montmorillonite (Mt), thus eliminating the drawback induced by iron contamination in the raw clay. Depending on the nature of intercalated molecules, it was proven that the interlayer space changes and sometimes the rearrangement of cation position also occurs (McAlpine et al., 2006; Hrachova et al., 2009; Piscitelli et al., 2010; Mishra et al., 2012).

Less interest was devoted to the possible modifications that could occur to Mt along the different processing steps of composites production. Mt has been extensively used as a filler for polymer reinforcement, both without any modification (Bourbigot et al., 2003; Bala et al., 2004; Essawy and El-Nashar, 2004; Hrachova et al., 2009; Carrera et al., 2013; Alekseeva et al., 2015) and after surface modification with Si-based materials (Song and Sandi, 2001; Shanmugharaj et al., 2006; Piscitelli et al., 2010). However, the literature reports only few studies devoted to the effect of both acid (Tkac et al., 1994) and basic (Takahashi et al., 2007) treatment, or to clay behavior under thermal treatment (Piscitelli et al., 2010). In any case, the past studies (Kooli, 2009) suggest that Mt is particularly sensitive to the processing conditions.

In order to provide some insight on the interaction between sonicated sodium montmorillonite particles (Mt) and organosilane-based network (Fedel et al., 2014), in this work the detailed characterization of sol-gel hybrid sodium montmorillonite-silica coatings was carried out by means of multinuclear solid state nuclear magnetic resonance and X-ray diffraction (XRD). Respect to the previous paper (Fedel et al., 2014), the present work is focused on assessing the contribution of both nanoclay sonication process and Mt/organosilica interaction on the final structural arrangement of the CON network. Following the procedure described by Fedel et al. (2014), the sol-gel films were obtained from a hydrolysed solution prepared from 3-glycidoxypropyltrimethoxysilane (GPTMS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) with 2 wt% of sodium montmorillonite. The effect of different sonication times (i.e. 0, 1, 3 and 12 h) on the structure of both pristine Mt and sol-gel clay-organosilica nanocomposite film was investigated. The physical chemical investigation revealed the effect of the different time of sonication on the Mt nanoparticles structure and consequently on the features of the sol-gel coatings, particularly the filler-matrix interaction. These structural differences translate into a different electrochemical response of the coatings, as previously demonstrated (Fedel et al., 2014).

2. Materials and methods

2.1. Materials

3-glycidoxypropyltrimethoxysilane (GPTMS) was supplied by Sigma–Aldrich, whereas tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) were supplied by VWR, and used without further purification. Cloisite Na, a sodium montmorillonite, was purchased from Southern Clay Products, USA. The interspacing distance value of 11.7 Å is reported in the reference data sheet of the product (Southern Clay Products Inc., Gonzales, Tx, USA, Product Bulletin/Cloisite®).

2.2. Samples preparation

The experimental procedure used for the coatings preparation was reported previously (Fedel et al., 2014). The Mt was ultrasonically dispersed in aqueous solution applying a continuous treatment for 0, 1, 3 and 12 h, respectively. The procedure was performed in a 50 ml beaker with a Hielscher UP100H sonicator with the power set to 13.5 W and controlled in temperature by using tap water circulation. After sonication, the pH of the aqueous dispersions containing 2 wt% of Mt was adjusted to 3.5 by adding hydrochloric acid. The Mt dispersion, sonicated for different time, was added to the silane mixture prepared with TEOS, GPTMS, MTES in 1/1/1 weight ratio (final Si content in the sols: 10 wt%) and the obtained mixtures were used for coatings preparation.

The layers were deposited onto Teflon sheets using a tape caster and cured in oven at 150 °C for 20 min. The cured films were peeled from the sheets and milled to obtain fine powders, which were used for X-ray diffraction (XRD) and solid-state nuclear magnetic resonance (NMR) analyses.

For studying the interaction of filler with both silica and silsesquioxane matrices, nanocomposite samples were obtained adding Mt to TEOS and GPTMS:MTES 1:1 solutions, respectively. Reference samples were prepared respectively from TEOS:GPTMS:MTES 1:1:1 sol, pure TEOS sol and GPTMS:MTES 1:1 sol, under the above reported conditions without clay addition. As described above, the prepared sols were used for coating Teflon substrates, and the layers were cured, peeled from the substrate and milled to obtain fine powders.

For analysing the effect of sonication on the pure filler, Mt was dispersed in water, sonicated for different time, and finally recovered and dried in air before the structural characterization. Table 1 summarizes sol synthesis conditions and sample labels used throughout the paper.

2.3. Characterization techniques

The MAS (magic angle spinning) NMR analyses were performed on a Bruker Avance 400WB spectrometer with a magnetic field of 9.4 T (“Klaus Müller” NMR Laboratory, University of Trento). ²⁹Si MAS spectra were recorded at the Larmor frequency of 79.49 MHz, with $\pi/2$ pulse length of 3.5 μ s, 90s recycle delay, and the acquisition of 4k scans. The spectra were recorded on samples packed in 4 mm zirconia rotors with a spinning rate of 8.5 kHz and using Q₈M₈ as external secondary reference (peaks at 12.6 and 108.0 ppm). The used recycle delay was set through several tests with increasing recycle delays in order to get reliable quantitative spectra. The Si structural units are labeled according to the usual NMR notation: Tⁿ and Qⁿ indicate SiCO₃ and SiO₄ silicon units, respectively and n is the number of oxo-bridges. The notation Qⁿ(mAl) is used for indicating the local Si environment in Mt, where m represents the number of tetrahedral Al atoms (i.e. Al(IV)) that are nearest-neighbours to Si. ²⁷Al MAS spectra were recorded at the Larmor frequency of 104.67 MHz, with $\pi/2$ Hahn-echo pulse length of 2.2 μ s, 3 s recycle delay, with acquisition of 1k scans. Samples were

Table 1
Synthesis parameters and sample labeling.

Sample labels	Composition (weight ratio)	Mt Sonication time, h
Mt0, 1, 3, 12	Na-montmorillonite	0, 1, 3, 12
SIL	TEOS:GPTMS:MTES = 1:1:1	–
Q _{SIL}	TEOS	–
T _{SIL}	GPTMS:MTES = 1:1	–
Q _{SIL} /Mt3	TEOS + 2%wt Mt	3
T _{SIL} /Mt3	GPTMS:MTES = 1:1 + 2%wt Mt	3
SM0, SM3, SM12	TEOS:GPTMS:MTES = 1:1:1 + 2%wt Mt	0, 3, 12

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