



Study of the effect of nanoclay incorporation on the rheological properties and corrosion protection by a silane layer

M.-G. Olivier^{a,*}, M. Fedel^b, V. Sciamanna^a, C. Vandermiers^a, C. Motte^c, M. Poelman^c, F. Deflorian^b

^a Université de Mons (UMONS), Faculté Polytechnique, Materials Science Department, Place du Parc 20, 7000 Mons, Belgium

^b Department of Materials Engineering and Industrial Technology, University of Trento, Via Mesiano 77, 38100 Trento, Italy

^c Materia Nova ASBL, Rue de l'Épargne 56, 7000 Mons, Belgium

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ABSTRACT

The corrosion protection properties offered to galvanized steel by an aqueous based silane layer are studied after incorporation of different amounts of sodium montmorillonite nanoclays (Na MMT). The rheological behaviour of Na⁺ nanoclays in aqueous suspensions was determined in order to select the appropriate sonication time and concentration for incorporation in the silane matrix. The effect of sonication on the disaggregation/exfoliation of platelets was evaluated by using different characterization methods such as using the methylene blue (MB) dye as a spectrophotometric probe (UV–vis), zeta potential and hydrodynamic diameter measurements.

The corrosion protection conferred to galvanized steel substrate by the modified silane layer was evaluated by electrochemical impedance spectroscopy (EIS) in 0.1 M aerated sodium chloride solution. The barrier properties of the silane layer are significantly increased by addition of 2 wt.% of clay sonicated for 1 and 2 h.

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1. Introduction

Due to their efficient properties as coupling agents, organosilane molecules are a very interesting environmentally friendly alternative to toxic chromate compounds used in conversion treatment baths for many metals [1–7]. Numerous studies [8–13] are reported in the literature which evidenced the corrosion protection properties conferred by these hybrid layers. This pretreatment offers a barrier against water and aggressive ion diffusion. Furthermore previous studies showed that nanoclays and clays are able to increase significantly the barrier properties of organic coatings and polymeric matrix by increasing the diffusion path length of the electrolyte through the coating [14–16]. The aim of this study is to improve the barrier properties of the silane sol–gel layer by incorporation of Na⁺ nanoclays. Nevertheless, this improvement is strongly depending on granulometric distribution, exfoliation state, dispersion and concentration of clays in the studied matrix [17,18]. In order to improve the exfoliation of platelets in the aqueous silane suspension the nanoclays are sonicated before layer application. Their corrosion performances are evaluated by using electrochemical impedance spectroscopy in 0.1 M NaCl solution after different immersion times. The sol–gel matrix used to embed the nanoparticles is an experimental mixture of three differ-

ent silane molecules: γ Glycidoxypropyltrimethoxysilane (γ GPS), Tetraethoxysilane (TEOS) and Methyltriethoxysilane (MTES). The balance between the different silane molecules provides a sol–gel film with adequate adhesion properties and flexible 3D network [19].

The rheological behaviour of aqueous suspensions of nanoclays is studied in order to select the appropriate concentration [20]. The stability of suspensions was checked by zeta potential and hydrodynamic diameter measurements for different sonication times. The effect of sonication on sodium montmorillonite (Na MMT) exfoliation/disaggregation was evaluated using the methylene blue (MB) dye as a spectrophotometric probe [21,22]. Due to their high absorption properties, dye molecules are easily detected by spectrophotometry (UV–vis). As a cationic dye, MB has a very high affinity for negatively charged clay surfaces and is readily adsorbed when added to clay suspensions. Depending on the different environments present on the individual clay particles or on clay particle aggregates, various molecular species of the dye can be formed during the adsorption process.

2. Experimental

2.1. Materials

The metallic substrates were cut from continuous hot-dip galvanized steel sheets (0.15 wt.% Al) supplied by ArcelorMittal (Belgium) and covered by the silane sol–gel film after etching. The

* Corresponding author. Tel.: +32 0 65374431; fax: +32 0 65374416.

E-mail address: marjorie.olivier@umons.ac.be (M.-G. Olivier).

etching solution for the activation of the surface before application of the coating was an alkaline degreaser (Gardoclean®, supplied by Chemetall, Germany). The organosilane molecules used were γ -Glycidoxypropyltrimethoxysilane (Sigma–Aldrich, 99% purity), Tetraethoxysilane (VWR, 98% purity) and Methyltriethoxysilane (VWR, 98% purity). These products were used as received without further purification. The neat clay mineral used as fillers was a sodium montmorillonite (Na MMT supplied by Southern Clay Products, USA), also called cloisite Na. The ion exchange capacity and the X-ray diffraction d -spacing were 92.6 mequiv./100 g and 11.7 Å, respectively.

2.2. Sample preparation

The galvanized steel sheets were cut to a size of 45 mm \times 50 mm and then degreased with acetone. The chemical etching was performed by dipping the samples in the alkaline degreaser for 30 s at 60 °C.

The clay nanoparticles were ultrasonically dispersed in an aqueous solution. Ultrasonic treatment was performed 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. The pH of the dispersion was properly modified (pH 3.5) adding hydrochloric acid. Different sonication times were investigated: 10 min, 30 min, 1 h, 2 h and 3 h respectively. Concentrations of 0.5, 1, 2 and 3 wt.% of Na MMT particles in the aqueous solution were tested.

The aqueous suspensions containing 2 wt.% of Na MM dispersed with different sonication times were added to 10 wt.% of silane molecules. The silane mixture consists of an equal weight percentage of each one of the three silane molecules. After rinsing in tap water and then in deionised water, the etched galvanized steel samples were dipped for 3 min in the different silane solutions. The withdraw rate is fixed at 0.2 m min⁻¹ for all experimental conditions. The sol–gel network is obtained for each sample by drying and curing at 180 °C for 15 min. The thickness of the layer estimated by XPS profilometry analysis is around 200–300 nm.

2.3. Experimental techniques

The rheological behaviour of aqueous suspensions of nanoclays maintained at pH 3.5 (with and without silane mixture) was determined by monitoring the flow curves, the apparent viscosity and the thixotropy behaviour obtained from the shear stress versus shear rate at 26 °C using a controlled rheometer (RS-150, Haake, Karlsruhe, Germany) with double gap cylinder geometry (DG-41) and equipped with a thermostat (TC501). The shear rate was linearly controlled between 0 and 200 s⁻¹ for 2 min. For thixotropy behaviour, the maximum shear rate (200 s⁻¹) is maintained for 2 min before the reverse measurement.

Dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments, Great Britain) was used to monitor the zeta potential and the hydrodynamic diameter of nanoclays in distilled water or in distilled water plus silane. These measurements gave information about the stability of suspensions and the silane/nanoclay compatibility. All measurements were carried out using disposable cuvettes: DTS0012 for sizing and DTS1060C for zeta potential measurements. The granulometric distribution between 0.2 μ m and 2 mm was checked by using a laser diffractometer (Mastersizer, Malvern Instruments, Great Britain).

The disaggregation/exfoliation rate for the different sonication times was estimated by UV/vis experiments using a Perkin-Elmer spectrometer (UV–vis spectrometer, type Lambda 14P, Perkin Elmer, USA) equipped with a 1.0 cm cuvette. A 10⁻⁵ M stock solution of methylene blue (MB) was prepared. Afterwards, 2 g/l Na MMT suspensions were prepared by diluting 0.5 ml of the different

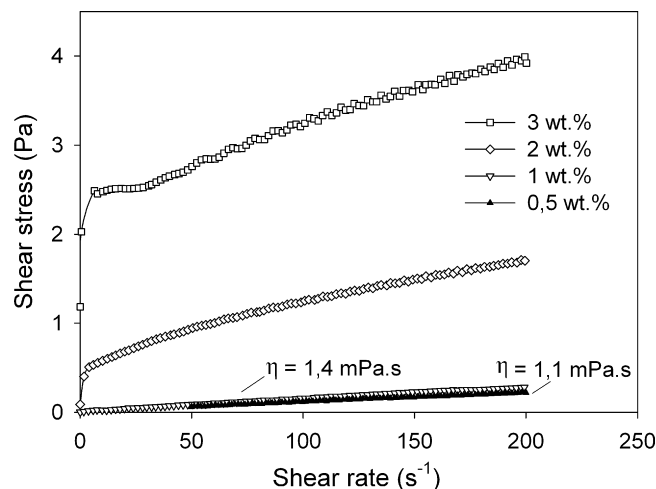


Fig. 1. Flow curves of Na MMT suspensions (0.5, 1, 2 and 3 wt.% of NaMMT in water – 26 °C, pH = 3.5).

2 wt.% sonicated clay suspensions (pH = 3.5) in 49.5 ml of the MB stock solutions (pH = 3.5).

Electrochemical impedance spectroscopy measurements were carried out on silane coated galvanized steel samples. A conventional three-electrode cell was used. The working electrode was the investigated sample. The counter electrode was a platinum plate and all potentials were measured with respect to an Ag/AgCl reference electrode (+197 mV/SHE). In order to minimize external interference on the system the cell was placed in a Faraday cage. The electrolytic solution was NaCl 0.1 M and the immersed area was 7.07 cm². The impedance measurements were performed over frequencies ranging from 100 kHz to 10 mHz using a amplitude signal voltage of 5 mV rms. The impedance spectra were obtained using a Parstat 2273 (Ametek) controlled by the Powersuite® software.

3. Results and discussion

3.1. Suspension characterization

Fig. 1 shows the rheological behaviour of 0.5, 1, 2 and 3 wt.% Na MMT aqueous suspensions after 1 h of sonication. Suspensions with 0.5 wt.% and 1 wt.% of Na MMT exhibit Newtonian behaviour and a viscosity close to that of water at the same temperature (1.1 and 1.4 mPa s, respectively). This behaviour is representative of a system showing no interaction between nanoparticles. The increase of the shear rate does not change the apparent viscosity. For higher concentrations (2 and 3 wt.%), the flow behaviour is pseudoplastic. The apparent viscosity decreases with the shear rate due to the alignment of the nanoclays in the shear direction and the breakdown of the Van der Waals interactions. The apparent viscosity is strongly raised at a same shear rate for a 3 wt.% concentration. In order to allow the formation of a 3D network in solution and to avoid a significant increase of the gel viscosity and the consequent formation of porous film, the lowest Na MMT content that leads to pseudoplastic flow curves was selected for further investigation. The effect of sonication time on the rheological behaviour was investigated and is presented in Fig. 2. Whatever the value of sonication duration, a pseudoplastic behaviour is observed and confirms the orientation of nanoclays in the shear direction. The thixotropy behaviour was evaluated by forward and reverse curves for different sonication times. Up to 1 h of sonication, the behaviour of suspensions is time-dependent as a thixotropic loop is observed. This loop means a reversible breakdown of the network structure under shear, followed by structural reformation on resting. Before

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