



# Scratch, wear and corrosion resistant organic inorganic hybrid materials for metals protection and barrier



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## ARTICLE INFO

### Article history:

Received 11 October 2014

Accepted 24 December 2014

Available online 5 January 2015

### Keywords:

Barrier materials

Metal protection

Grafting

Inorganic polymers

Manufacturing

## ABSTRACT

Polysiloxanes are widely used as protective barriers to delay erosion/corrosion and increase chemical inertness of metal substrates. In the present work, a high molecular weight methyl phenyl polysiloxane resin was designed to manufacture a protective coating for Fe 430 B structural steel. Methyl groups feature very small steric hindrance and confer ductility to the Si–O–Si backbone of the organic inorganic hybrid resin, thus allowing the achievement of high thickness. Phenyl groups feature larger steric hindrance, but they ensure stability and high chemical inertness. Visual appearance and morphology of the coatings were studied by field emission scanning electron microscopy and contact gauge surface profilometry. Micro-mechanical response of the coatings was analyzed by instrumented progressive load scratch, while wear resistance by dry sliding linear reciprocating tribological tests. Lastly, chemical inertness and corrosion endurance of the coatings were evaluated by linear sweep voltammetry and chronoamperometry in aggressive acid environment. The resulting resins yielded protective materials, which feature remarkable adhesion to the substrate, good scratch resistance and high wear endurance, thus laying the foundations to manufacture long lasting protective barriers against corrosion and, more in general, against aggressive chemicals.

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## 1. Introduction

The design of coatings to protect metal substrates from corrosion is of high relevance in several industrial segments including construction, manufacturing, aeronautic, chemical and petrochemical. Good protection is achievable by the design of coatings, which feature chemical composition inert in saline, acid and alkaline environments. In addition, protective coatings should feature high barrier properties to the potentially corroding agents through high thickness and low porosity of the surface overlying coating. Lastly, protective coatings should firmly adhere to the metal substrate through the establishment of solid covalent bonds to avoid or retard the infiltration of corroding species at the interface metal/coating.

Organo-silane barrier coatings are often reported in the pertinent literature for the design and manufacture of protective layers on metals [1–5]. They ensure outstanding adhesion to metal substrates as they can establish solid covalent bonding of their alkoxy groups with the hydroxyl counterparts often found on the activated metal substrates. Chemical inertness is ensured by the

Si–O–Si network. Nevertheless, the high inorganic fraction confers to these coatings a glassy-like behavior. The coatings are thus very brittle and they can be applied on the metal substrate with very low thickness of 1 or few microns [1]. Thicker coatings would spontaneously delaminate from the substrate due to the differential shrinking between metal/coating during the drying of the organo-silane layer. The differential shrinkage would induce high residual stresses inside the coating, which could overcome the ultimate strength of the organo-silane material, thus determining the onset of large fractures and, occasionally, coating delamination [2,3]. Although the superior chemical inertness of the Si–O–Si bonds, organo-silane coatings, which feature high inorganic fraction, see their barrier properties against corrosion agents strongly limited by the low thickness the intrinsic fragility of the material imposes during the deposition and cross-linking process [4,5].

Organo-silane barriers can be improved by modifying the coating structure and inserting in the Si–O–Si network a large organic fraction [6–11]. The organic groups confer additional ductility to the organo-silane layer, despite they reduce their chemical inertness against many aggressive chemicals [6]. Jovanovic et al. investigated the chemical endurance in saline environments of methacryloxypropyltrimethoxysilane films on aluminum [7], finding a resistance limited to few days despite the blunt testing conditions (3 wt.% NaCl).

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Mohseni et al. [8], first, and Zand and Mahdavian [9], later, showed the effect of epoxy groups to modify organo-silane networks. The epoxy groups conferred improved ductility and toughness to the protective coating. Nevertheless, the improvement of the protection against corroding agents was not satisfactory [8,9]. In fact, the critical thickness at which the organo-silane barriers can be applied on the metal to protect is not the unique issue, which can affect their performance. The feature of the functional groups on the silane network [10,11], pre-hydrolysis time to build the network [12], molar ratio between resin and silane precursor [13] or between different silane precursors [2,11,13–15] and degree of crosslinking achievable in the organic and inorganic fraction of the resin [14,15] can influence the performance of the protective coatings and decrease anti-corrosion properties.

Alternative routes would include the addition of nano-particles to the protective coating based on organo-silane compounds. The nano-particles should increase the mechanical response of the coating, improve the sealing of the coating against water-driven corroding species and retard the corrosion process in case the particles act as corrosion inhibitor, too. [16,17]. Protective coatings manufactured with 3-glycidox showed good resistance in saline fog (3.5 wt.%, NaCl) at environmental temperature before cracking. However, the testing conditions were very blunt to assess the reliability of these coatings [17].

To overcome the intrinsic limit of the organo-silane coatings, polysiloxanes have been recently introduced as alternative routes to the corrosion protection of metal substrates. They can be easily designed to include a large organic fraction which, if appropriately, balanced can ensure good toughness and ductility of the coating, without compromising the chemical inertness and stability of the material [12,18]. Qian et al. investigated the effectiveness of protective barriers based on modified epoxy silicone resin cross-linked with amino-silane hardener in saline, acid and alkaline environments [10]. They showed significant advance in the anti-corrosion features of the resin in comparison with organo-silane barriers. However, the main drawbacks of this material was the reduced reactivity with the metal substrate, which limited the interfacial adhesion leaving chance to corroding agents (especially, the hydroxyl ions in alkaline environments) to infiltrate at the interface metal/substrate and compromise the performance. The limited adhesion was ascribed to the steric hindrance of the large epoxy modified silicone resin, which limits the reaction, by hydrolysis and condensation of the resin functional groups (alkoxy) with the corresponding hydroxyl counterpart on the metal substrate. In the present investigation, an alternative to epoxy silicone resin, that is, a high molecular weight methyl phenyl resin is proposed to manufacture a protective coating for Fe 430 B structural steel. Methyl groups feature very small steric hindrance and confer ductility to the Si–O–Si backbone of the organic inorganic hybrid resin, thus allowing the achievement of high coating thickness. Phenyl groups feature larger steric hindrance, but they ensure stability and high chemical inertness. The resulting resins yielded to protective coatings, which feature a remarkable adhesion to the substrate through the easier formation of Si–O–M bonds through reactions of hydrolysis and condensation between the alkoxy groups on the resin and the hydroxyl groups on the metal. Good scratch resistance and high wear endurance are thus achieved, laying the foundations to manufacture long lasting protective barriers against corrosion and, more in general, against aggressive chemicals.

## 2. Experimental Details

### 2.1. Materials

The substrates are flat slabs in structural Fe 430 B steel 40 mm long, 30 mm wide and 5 mm thick. The hybrid organic-inorganic

resin is a modified methyl phenyl polysiloxane (Evonik, Essen, Germany) functionalized with hydroxyl and alkoxy groups on the sides of the main Si–O backbone. Additives like thickeners, flow promoters, wetting agents and defoamers complete the formulation. The organo-silane is a vinyltriethoxysilane (VTEO, Evonik, Essen, Germany), selected as it can offer an array of hydrolysable alkoxy groups plus the cross-linkable organic vinyl group. Metal pigments are commercially available finely sieved Al–Mg (4.5 wt.%) powders (Eckart, Uden, The Netherlands) ~10 µm average diameter of the granulometric distribution, ~0.90 shape factor.

### 2.2. Manufacturing process

Metal substrates were pre-treated by a lapping machine with sandpaper (Al<sub>2</sub>O<sub>3</sub> 400 mesh size) until the achievement of a fairly smooth and homogenous morphology. Pre-treated substrates were washed in an ultrasonic bath of isopropyl alcohol, followed by an additional washing in a solution of an alkaline detergent in demineralized water. The substrates were rinsed with bi-distilled water and dried overnight at 60 °C in a vacuum oven to prevent substrate oxidation. Pre-treated substrates were sprayed (2 bar feeding pressure, nozzle 0.8 mm, stand-off distance 400 mm) with diluted polysiloxane resins with or without the metal pigments dispersed inside or with a pre-hydrolyzed solution of vinyltriethoxysilane (2 wt.%) in ethanol (96%) and demineralized water. In the former case, the coated substrates were pre-dried for few minutes at environmental conditions (~20 °C and 40% HR) and subsequently baked in convection oven at 250 °C for 45 min to cross-link the polysiloxane resin. In the latter case, the organo-silane interlayers were pre-dried for few minutes at environmental conditions (~20 °C and 40% HR) and subsequently baked in convection oven at approximately 100–110 °C for 10 min to achieve the full consolidation of the primer. The organo-silane coated metal substrates were then recoated with a second layer of the polysiloxane resin. Pre-drying for few minutes at environmental conditions (~20 °C and 40% HR) and subsequent baking in convection oven at 250 °C for 45 min completed the latter deposition process. All the manufactured coatings are summarized in Table 1. Four reference samples in Fe 430 B, uncoated or Zn coated (deposited by hot dipping, cold spraying, electro-galvanizing), with layers of equivalent thickness to the above mentioned hybrid organic inorganic coatings, was used for comparative purposes.

### 2.3. Experimental procedure

Coatings thickness and their uniformity was measured by a magnetic inductive gauge (Mega-Check 5FN-ST, List-Magnetik, Leinfelden-Echterdingen, Germany), performing nine measurements equally distributed over the coated surface. The coatings thickness was always designed to fall within the prescribed range of 60–80 µm. In the case of double-layered samples, all the layers were designed to fall within the range of 30–40 µm to get to final coating thickness included in the prescribed range of 60–80 µm. All the samples that failed to agree with the aforementioned specifications were disregarded.

Cross-cut tape test method according to the ASTM: D3359 regulation and pencil test method according to the ASTM: D3363 regulations were performed to evaluate the coatings adhesion to the substrate and their hardness.

Coatings morphology was analyzed by contact inductive gauge of a CLI profiler (TalySurf CLI 2000, Taylor Hobson, Leicester, UK). In particular, 2000 profiles, 4 mm long, were stored for each sample, with the resolution of 1 µm along the measurement direction, covering an area 4 × 4 mm<sup>2</sup>. Stored profiles were elaborated using the TalyMap 3.1 software, and main roughness parameters were evaluated. A Field Emission Gun – Scanning Electron Microscope (FEG-

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