



Synthesis of polypyrrole-magnetite/silane coatings on steel and assessment of anticorrosive properties



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ABSTRACT

This work presents a detailed study of the synthesis of polypyrrole-magnetite/silane coatings (PPy-Fe₃O₄/GPTMS-TEOS-γ-APS) and their anticorrosion properties. The use of a bilayer system is proposed consisting of a PPy-Fe₃O₄ internal conductive coating (active coating), obtained electrochemically, and an outer coating or insulating barrier consisting of silanes (passive coating). This latter is composed by Tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTMS) and γ-aminopropyl-silane (γ-APS). The GPTMS-TEOS-γ-APS hybrid was obtained by the sol-gel method and applied by the dip coating technique. The anticorrosive properties of the PPy-Fe₃O₄/GPTMS-TEOS-γ-APS bilayer coating applied on carbon and stainless steel substrate were assessed by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and Raman spectroscopy. The electrochemical characterization has shown that the anodic polarization of the substrate by the conductive polymer was beneficial for the carbon steel substrate whereas it induced pitting corrosion to stainless steel. It was also demonstrated that the addition of Fe₃O₄ to the PPy matrix slows down its reduction rate increasing its stability and that the presence of a barrier top-coat (like a silane film) is fundamental to preserve the effective anticorrosion performance of the PPy-Fe₃O₄ composite coating for long term exposure.

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1. Introduction

In recent years, silane coatings have been used extensively in the corrosion control of metals. In general, these coatings are known as “passive” because in the beginning they essentially act as a physical barrier that prevents water, oxygen and corrosive ions from reaching the metal substrate. Essentially they do not exhibit active corrosion properties and do not heal micro-defects or improve their performance when the coating is saturated by the electrolyte [1].

However, a silane film alone cannot effectively protect metals against corrosion for a long time due to its low thickness, becoming quickly saturated with the electrolyte and losing its barrier effect [2]. Due to this fact numerous studies have focused on investigating more complex systems such as metal/silane/organic coatings, where the integrated system operates in the same manner as a physical barrier but with superior performance. It is generally accepted that protection using barrier coatings comprises cathodic polarization as a result of the limited permeation of oxygen and water. Polarization resistance results from the electrical resistance

of the coating and anodic polarization is a consequence of the migration of restricted metallic ions through the coating [3,4]. Such systems have shown positive results in terms of protection of different metallic substrates exposed to corrosive environments. The silane addition acts as a barrier and its main role is to contribute to improving the adhesion between the metal substrate and the organic coating, as is the case with epoxy resins [5], polyimides [6] and epoxy/polyamide mixtures [7], etc. Previous studies have shown that a GPTMS-TEOS-γ-APS coating based on silanes exhibits protective properties on carbon steel [8]. However, a coating system is not impervious indefinitely. Once the electrolyte reaches the interface corrosion occurs on metal substrate, which can result in delamination between the coating and the protected metal. Therefore, the protective efficiency of a coating is generally related to its barrier performance against water, oxygen and corrosive ions. It can also be related to the active role it plays as an intermediate layer between the barrier coating and the metal substrate. In this way, it may interfere with the corrosive process through self-healing in the presence of defects or pores that allow the entry of corrosive agents.

Thus, the interfacial layer formed below the base coating of silanes plays an important role in the process of inhibiting further corrosion. The compactness and character of this intermediate layer formed between the sol-gel coating and the metal substrate is very

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important with respect to corrosion protection, since the breaking of the film provides the direct entry of corrosive agents to the metal surface. Because of this, a silane coating must be modified or complemented with other protection systems in order to improve its barrier effect and preserve its anticorrosion properties over a long time. Numerous research papers related to apply electroconductive PPy coatings on steel in the presence of oxalic acid have shown the benefits of this intrinsic conductive polymer as a protective coating for ferrous metals [9–14]. However, there is not enough evidence in the literature in terms of the interaction between the substrate and the polymer through galvanic coupling and the anodic polarization of the substrate to state that PPy provides corrosion protection of steel substrates [15–18].

This work presents a detailed study of synthesis of polypyrrole-magnetite/silane coatings and their anticorrosion properties. It proposes the use of a PPy-Fe₃O₄ internal conductive coating (active coating) as an intermediate layer between the metal and a coating based on silanes (passive coating). It was expected that the polypyrrole (PPy) would act as an anodic polarizer by keeping the metal in the passive state [19]. The role of the magnetite particles in the polymer matrix is to stabilize this latter, as was demonstrated in previous studies [20]. With this configuration, coatings may then be obtained with a component which offers active protection that can interfere in the reactions inherent to corrosive processes. The use of a hybrid silane (upper layer passive component) is expected to increase the barrier properties and the protective capacity of the PPy-Fe₃O₄ composite coating for a longer time and decrease the penetration of aggressive species that promote corrosion when the coated metal is exposed to a corrosive environment.

2. Experimental

2.1. Surface preparation of the substrates

Carbon steel (CS) AISI 1020 and 304 stainless steel (SS) disks of 15 mm in diameter were used as substrates. Surface pretreatment of the samples was required in order to enhance the adherence of the coatings. This procedure began with a mechanical grinding to grade 600 with silicon carbide emery paper followed by degreasing in an ultrasonic bath with organic solvents of different polarity: *n*-hexane, acetone and methanol, for 15 min each. Finally the substrate was activated by immersion in a 25% KOH and 2% EDTA solution for 30 min.

2.2. Electrodeposition of PPy and PPy-Fe₃O₄ coatings

The experimental procedure carried out to obtain the PPy-Fe₃O₄ coatings comprised the following steps.

Pyrrrole (Py) monomer (reagent grade, Aldrich) was purified by vacuum distillation and stored below 0 °C. All other reagents, including oxalic acid, NaHCO₃ and Na₂SO₄ were reagent grade and used as received. All the solutions were prepared with ultrapure water (0.054 μS cm⁻¹). The PPy and PPy-Fe₃O₄ coatings were obtained by galvanostatic polarization applying a current density of 1.13 mA cm⁻² at room temperature in a three-electrode cell. A platinum mesh was used as counter electrode and an Ag/AgCl (0.1 mol L⁻¹ NaCl) electrode as reference. CS and SS disks of 15 mm in diameter were used as working electrodes. The electrolyte employed in the synthesis of the PPy and PPy-Fe₃O₄ coatings was a 0.1 mol L⁻¹ pyrrole and 0.1 mol L⁻¹ oxalic acid solution or a 0.1 mol L⁻¹ pyrrole and 0.2 mol L⁻¹ Na₂SO₄ solution. Electrodeposition of the coatings was carried out immediately after the surfaces were properly pretreated. The coatings were obtained in two stages:

- (1) Electrodeposition of the PPy coating from the 0.1 mol L⁻¹ pyrrole and 0.1 mol L⁻¹ oxalic acid solution. The pH of the electrolyte was previously adjusted to 2.4 with NaHCO₃ and the electrodeposition time was found to be 600 s.
- (2) Electrodeposition of the PPy-Fe₃O₄ coating from the 0.1 mol L⁻¹ pyrrole and 0.2 mol L⁻¹ Na₂SO₄ solution containing Fe₃O₄ particles dispersed in the electrolyte. The electrodeposition time of this stage was experimentally found to be 1200 s.

Both stages were carried out by applying a constant current density of 1.13 mA cm⁻². The only difference between the PPy and PPy-Fe₃O₄ coatings was the presence of Fe₃O₄ in the second stage of the synthesis for the latter. There are two important reasons for using different electrolytes in each stage of these coatings production; the first is to avoid the dissolution of the metal in Na₂SO₄ and the second to avoid the dissolution of the magnetite particles in the oxalic acid. Thus, a first layer of PPy was obtained in oxalic acid to protect the metal from subsequent dissolution and then a second layer of PPy was attained containing the magnetite particles dispersed within the coating. Prior to electrodeposition, Fe₃O₄ particles were dispersed in the electrolyte using high intensity ultrasonic radiation for 30 min, by employing a direct immersion titanium probe (20 kHz, 10 W cm⁻¹) that was dipped into the solution to a depth of 1 cm.

2.3. Application of GPTMS-TEOS-γ-APS coatings

The procedure followed for the preparation of the TEOS (Tetraethoxysilane) – GPTMS (Glycidoxypropyltrimethoxysilane) – γ-APS (γ-aminopropyl-silane) hybrid is similar to that described by Segura et al. [8] and Khramov et al. [21], where γ-APS was used as a crosslinking agent. For the synthesis of the hybrid, TEOS and GPTMS (1:3 mol ratio) were first mixed with distilled water and ethanol (95:5). Subsequently, the pH of the mixture was adjusted to 4.0 with acetic acid. This solution was then hydrolyzed at room temperature for 48 h with constant stirring. The final sol-gel solution was prepared by diluting the hydrolyzed TEOS-GPTMS in water by a factor of 1.75, followed by the addition of a nonionic surfactant (Nonyl Phenol 9.6 EO 60) and the crosslinking agent (γ-APS). The molar ratio of γ-APS to GPTMS was kept constant by a ratio of 1:0.15. Once the TEOS-γ-APS-GPTMS mixture had been hydrolyzed for 30 min, the coating was applied by dip coating at an immersion speed of 4 cm min⁻¹, a residence time of 60 s and a withdrawal rate of 2 cm min⁻¹. The coating was then cured at 120 °C for 1 h under nitrogen atmosphere in order to prevent the degradation of both the PPy and magnetite particles.

The successful application of the coatings described in the two previous sections was verified by contact angle measurements using the sessile drop method using a Ramé-Hart contact-angle goniometer, Model 100-10. Water drops were employed in these measurements. The distribution and uniformity of the silicon from the silane were studied by SEM Jeol, JSM-7401F. Raman spectroscopy analyses (HORIBA-Jobin-Yvon spectrometer system with 632.81 nm excitation from a He-Ne laser source.) were performed in order to characterize the condensed and cured GPTMS-TEOS-γ-APS hybrid film.

From now on the following nomenclature will be used for the different tested systems: degreased steel with organic solvents (degreased), steel activated by immersion in basic solution (BT), steel coated with PPy (PPy), steel coated with PPy and magnetite (PPy-Fe₃O₄), steel coated with GPTMS-TEOS-γ-APS hybrid (GPTMS), steel coated with a PPy/GPTMS-TEOS-γ-APS bilayer (PPy/GPTMS) or (PPy-Fe₃O₄/GPTMS) if the PPy matrix contains magnetite particles.

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