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Effect of silica/PVC composite coatings on steel-substrate corrosion protection

Marjetka Conradi [a,*], Aleksandra Kocijan [a], Milena Zorko [b], Ivan Jerman [b,c]

[a] Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
[b] National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
[c] CO-NOT, Hajdrihova 19, Ljubljana, Slovenia

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ABSTRACT

In this paper we focus on the preparation of thin polymer coatings synthetized from 30-nm and 600-nm silica particles dispersed in polyvinyl chloride (PVC) and deposited on two different steel substrates: duplex DSS 2205 and austenitic AISI 316L steel. We show that a silica surface modification with silane $IO_7T_7(OH)_3$ (trisilanol isooctyl polyhedral oligomeric silsesquioxane, POSS) significantly improves its dispersion properties when mixed with PVC. For comparison, the surface morphology and surface roughness of PVC coatings filled with both silanated and as-received (non-silanated) silica fillers were analyzed with scanning electron microscopy (SEM) and atomic force microscopy (AFM) when sprayed on the steel surface. The effect of the silica silanization is later on reflected in a decreased average surface roughness in the silanated, compared to non-silanated, silica/PVC-coatings. The wetting properties of the silanated and non-silanated silica/PVC-coatings on DSS 2205 and AISI 316L were investigated using contact-angle and surface-energy measurements, indicating an increased surface hydrophilicity in terms of a decreased static water contact angle and an increased total surface energy compared to the uncoated specimens. Finally, the beneficial corrosion resistance of the silica/PVC coatings was confirmed with potentiodynamic polarization spectroscopy in a 3.5% NaCl solution.

1. Introduction

Reducing the total costs and environmental consequences of corrosion problems have become a major challenge to engineers [1]. Austenitic (AISI) and duplex (DSS) stainless steels are very important engineering materials, due to their generally high corrosion resistance combined with favourable mechanical properties, such as high tensile strength [2,3]. The high corrosion resistance of the stainless steel is attributed to the presence of a passive film, which is stable, invisible, thin, durable and extremely adherent and self-repairing [2]. However, in many aggressive environments, such as a chloride-ion-rich environment, AISI is still observed to suffer from pitting corrosion in [1] and DSS is observed to be susceptible to crevice corrosion and stress corrosion cracking, especially in seawater, when the components are submerged [4].

Therefore, in the last two decades, the modification of metallic surfaces by various coatings, organic or polymeric, has become part of an important procedure for enhancing the surface properties, such as scratch resistance, oxidation and corrosion. Corrosion protection coatings on metallic substrates provide an effective physical barrier between the metal and its environment containing aggressive species, such as enhanced chloride ion concentration, O_2 or H^+.

A variety of polymers have been known to serve for metallic surface protection, including epoxy resins [5,6], polyesters [7,8] and polyurethanes [9,10]. Intrinsically conducting polymers, such as polyanyline, polypyrrole or polythiophene [11–14], have been employed for advanced anticorrosion protection through their redox catalytic properties, leading to the formation of a metal oxide passivation layer on the metallic surface. However, such polymer coatings are not permanently resistant. Once the coating is physically damaged, the aggressive ions have a free path to attack the metallic surface underneath, resulting in localized corrosion.

To further improve the anticorrosion properties of polymer coatings, recently, different inorganic additives have been successfully incorporated into the polymer matrices. This research has been most widely focused on filling polymers with either layered clay or various nanoparticles. It has been shown that a uniform dispersion of clay in different polymer matrices, i.e., polyaniline, polypyrrole, polythiophene, epoxy, polyimide, polystyrene, and polymethyl methacrylate [15–18], significantly decreases the permeability of the coatings, and therefore increases the lifetime of coatings as well as of metallic substrates. A uniform dispersion of nanoparticles (i.e., SiO_2), on the other hand, increases the surface hydrophobicity (i.e., a self-cleaning effect) and improves the

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[*] Corresponding author at: Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia. Tel.: +386 1 4701 972; fax: +386 1 4701 939.
E-mail address: marjetka.conradi@imt.si (M. Conradi).

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adhesion between the composite coating and the metallic surface [19].

Polyvinyl chloride (PVC) is one of today's well-known polymer materials that is used in a variety of applications, such as window frames, pipes, electric cables, etc. In the past few years, considerable attention has been devoted to toughening PVC by filling the polymer matrix with layered clay [20] or inorganic particles such as silica [21] because they act as excellent stress concentrators due to their different elastic properties compared to the matrix polymer. In spite of the favourable mechanical and optical (i.e., transparency) properties of PVC-based composites, not much attention has been paid to the development of PVC-based composite protection coatings.

In this paper we focus on the preparation of corrosion protection silica/PVC coatings and examine the corrosion protection effect of coated steel surfaces of the types DSS 2205 and AISI 316L in a chloride-ion-rich NaCl solution. We optimize the silica dispersion in PVC by silanization and follow with a thin-layer coating deposition using a simple spray-on method. We characterize the so-prepared coatings in terms of topography, morphology and thickness. The anticorrosion properties of composite coatings are tested with contact-angle/surface-energy and potentiodynamic measurements in a 3.5% NaCl solution.

2. Experimental

2.1. Steel substrate preparation

The substrates under investigation were duplex DSS 2205 stainless steel (22.7% Cr, 5.7% Ni, 2.57% Mo, 1.37% Mn, 0.38% Si, 0.032% P, 0.03% C, 0.001% S in mass fraction) and austenitic AISI 316L stainless steel (17% Cr, 10% Ni, 2.1% Mo, 1.4% Mn, 0.38% Si, 0.041% P, 0.021% C, <0.005% S in mass fraction).

The starting materials were cut into discs of 15 mm diameter and 1 mm thickness and prepared by a mechanical procedure, initially ground with SiC emery paper down to 1200 grid, prior to the electrochemical studies, and then rinsed with distilled water.

2.2. Coating preparation

Polyvinyl chloride (PVC, Aldrich)-based composite coatings were prepared by blending a PVC-tetrahydrofuran solution with 1% mass ratios of 600-nm and 30-nm SiO_2 particles. Tetrahydrofuran (THF, Aldrich) served as a solvent for the PVC. The 600-nm silica nanospheres were synthesized in our laboratory following the Stöber–Fink–Bohn method [22,23] and the 30-nm silica nanospheres were provided by Riedel-de Haën (Silica Cab-osil). To prevent agglomeration, silica particles were initially treated with $IO_7T_7(OH)_3$ (trisilanol isooctyl polyhedral oligomeric silsesquioxane, POSS) [24]. A homogeneous dispersion of the silica/PVC-THF mixture was then prepared by ultra-sonification for approximately 20 min. Finally, for the steel substrate protection, 150 μl of the dispersion was sprayed onto the steel surface with a simple spray nozzle and allowed to adhere in air during the THF evaporation process.

2.3. Scanning electron microscopy (SEM)

The morphological properties of the silica/PVC-coated steel surface were analyzed with a FE-SEM Zeiss SUPRA 35VP scanning electron microscope at an accelerating voltage of 1 kV.

2.4. Atomic force microscopy (AFM)

AFM was used to study the surface roughness and the average thickness of the silica/PVC coatings on steel substrates. The AFM images were obtained in air at room temperature on a NanoScope V multimode instrument (Veeco-Bruker/Digital Instruments, Santa Barbara, California) equipped with a 12-μm scanner. To probe the surface, the tapping mode was employed using a silicon tip with a force constant of 57 N/nm and a resonance frequency of 364 kHz. The scanned area of all the samples was 10 μm × 10 μm.

NanoScope software version 5.12r5 was used for both the image processing and the roughness analysis. The Veeco NanoScope software offers the possibility to calculate the average surface roughness, R_a, for each sample from the AFM surface topographic data in a scanning area of 10 μm × 10 μm (as set by the operator) using the equation:

$$R_a = \frac{1}{MN}\sum_{i=1}^{M}\sum_{j=1}^{N}\left|Z(x_i, y_j)\right| \tag{1}$$

where $Z(x_i, y_j)$ denotes the height of a surface point (x_i, y_j) relative to the mean plane and MN is the number of points in the analyzed area.

2.5. Contact angle and surface-energy measurements

The static contact-angle measurements of water (W), formamide (FA) and diodomethane (DIM) on the silica/PVC composite coatings prepared on steel (DSS 2205 and AISI 316 L) were performed on a DSA 100 contact-angle goniometer (Krüss, Germany), which works on the principle of the goniometer-sessile drop technique. Liquid drops of 8 μl were deposited on different spots of the coated substrates to avoid the influence of roughness and gravity on the drop shape. The drop contour was analyzed from the image of the deposited liquid drop on the surface and the contact angle was determined by using the Young–Laplace fitting. To minimize the errors due to roughness and heterogeneity, the average values of the contact angles of the drop were calculated 30–60 s after the deposition from at least five measurements on glass plates and from at least ten measurements on the studied coated steel. All the contact-angle measurements were carried out at 20 °C and ambient humidity. Van Oss and co-workers' approach [25] was used for the determination of the total surface free energy of the coating.

2.6. Potentiodynamic measurements

The corrosion stability of the investigated coatings was measured in 3.5% NaCl solution. In the experiment, the specimens with an exposed area of 1 cm^2 were embedded in a Teflon PAR holder, immersed into the solution and employed as a working electrode. A high-purity graphite rod served as the counter electrode and Ag/AgCl as the reference electrode. Potentiodynamic measurements were recorded using an EG&G PAR PC-controlled potentiostat/galvanostat Model 263 with M252 and Softcorr computer programs. The specimens were immersed in the solution 1 h prior to the measurement in order to stabilize the surface at the open-circuit potential. The potentiodynamic curves were recorded, starting at 250 mV more negative than the open-circuit potential. The potential was then increased, using a scan rate of 2 mV s^{-1}, until the transpassive region was reached. The polarization resistance values were approximated from potentiodynamic measurements near the corrosion potential, the corrosion rates were calculated using Faraday's Law according to the ASTM G102-89 (2010) (Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements).