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Effects of nanoparticulate silver on the corrosion protection performance of polyurethane coatings on mild steel in sodium chloride solution

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ABSTRACT

Waterborne polyurethane (WPU) and high solid polyurethane (HPU) coatings containing nanoparticulate silver were coated on mild steel and compared to the corresponding coatings without nanoparticulate silver in NaCl solution using electrochemical impedance spectroscopy (EIS). The EIS results showed WPU coating degradation in the presence of nanoparticulate silver, while inclusion of nanoparticulate silver in HPU coating revealed no significant effect on the coating resistance. The WPU and HPU coatings morphology was investigated by SEM cross-section, which showed loss of WPU coating integrity in the presence of nanoparticulate silver, while no significant effect was observed for the HPU coating. The dual behavior of nanoparticulate silver in WPU and HPU coatings was connected to their different chemical structures confirmed by FTIR spectroscopy.

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1. Introduction

Coatings are used for protecting metallic surfaces against corrosion, environmental degradation as well as biodegradation. The resistance of coatings to biodegradation and corrosion is important in food industries, buried pipelines in soil, marine structures, and wastewater treatment system. In these environments coatings may get in contact with different kinds of bacteria, salts, alkaline and acidic conditions.

There is a large literature related to incorporation of nanoparticles in organic coating in order to enhance anticorrosion performance. The effect of organically modified montmorillonite (OMMT) nano-clay and different types of modified clays on the corrosion resistance of different coatings was studied by EIS [1–4]. The possible reason for increment of the corrosion resistance of the coatings in the presence of different kind of nanoclays is connected to plate like structure of nanoclays, which can prevent the penetration of electrolyte through the coating by increasing the tortuosity of the penetration path consequently prevent the corrosion by barrier mechanism [2,5,6]. Another nanoparticles such as TiO_2 [7], ZnO [8,9], Fe_2O_3 [10], $CaCO_3$ [11], SiO_2 [12–14], carbon black nanoparticles [15] and multi-walled carbon nano-tubes [16], were perused for their corrosion resistance properties in different coatings.

Different mechanisms are proposed for the influence of nanoparticles on the corrosion protection performance of the coatings. Nanoparticles due to their small sizes can fill the coating's microholes formed from local shrinkage during curing of the coating leading to decrease of coating free volume and cross-linking density increment [14]. Nanoparticles have a high specific surface area in comparison with micro particles. It is believed that nanoparticles, taking advantage of their high specific surface area, numerously present within the coatings even at relatively low loadings leading to increase of the interaction of diffusing water with the particles surface [7]. Nanoparticles can adsorb more resin on their surfaces which decreases the free volume of the coatings leading to reduction of transport paths for the corrosive species [10].

In almost all the above-mentioned works, it is shown that incorporation of nanoparticles in the coatings could improve mechanical, thermal and electrochemical properties of the coatings. The impact of the mentioned nanoparticles on anticorrosion properties is mainly through barrier protection mechanism.

Taking advantage of biocides in coatings could prevent or delay the coating biodegradation. Different type of biocides can be used in the coatings, e.g., Cu_2O, 1-(3,4-dichlorophenyl)-3,3-dimethylurea (Diuron), cuprous thiocyanate, arsenic trioxide,

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4-chloro-meta-cresol [17], synthetic and natural zeolites and metal ions (Ag, Cu, Zn, Hg, Ti, Ni, Co). The use of metal nanoparticles in coatings to introduce antibacterial effect is relatively new [18]. More recently, several nanomaterials including Ag [19], TiO_2 [20], ZnO [21], WO_3 [22], and Cu [23] have shown the strong antimicrobial properties in the coatings. According to the results, the antimicrobial activity of silver is much higher than other metals such as copper, mercury, tin, chromium, and lead [9]. Although the influence of nanoparticulate silver as a biocide on biodegradation of the coatings is widely investigated and reported, there is no record on the effect of nanoparticulate silver on the corrosion protective performance of the coatings.

In the previous work the effect of nanoparticulate silver on antibacterial and thermal properties of waterborne and high solid polyurethane coating was studied [24,25]. It was shown that nanoparticulate silver has significant antibacterial effect in the polyurethane coatings and it improves the thermal stability of the coatings. However, the effect of silver nanoparticles on corrosion protection of the polyurethane coatings is unknown and not reported elsewhere. This work intends to study the effect of nanoparticulate silver incorporation in waterborne polyurethane (WPU) high solid polyurethane (HPU) coatings on corrosion protection performance.

2. Experimental

2.1. Material

Polyisocyanates for waterborne and high solid coatings were obtained from Bayer (Bayhydur 3100, 17.4% NCO, 100% solid) and BASF (Basonat HI 100, 22% NCO, 100% solid), respectively. Bayhydrol A 145 (1.5% OH, 45% solid) and Desmophen 670 (4.3% OH, 100% solid) were obtained from Bayer to be used in waterborne and 100% solid polyurethane coatings.

A nanoparticulate silver dispersion in ethanol (3780 ppm, confirmed by ion coupled plasma) with an average diameter of 50 nm (confirmed by TEM) was obtained from Sharif Nano Pigment Co.

2.2. Preparation of nanocomposite coatings

Nanoparticulate silver dispersion was added into the acrylic components of polyurethane coatings in different portions to obtain 100, 200 and 300 ppm by weight (mg/kg) in the final dry polyurethane films. The ultrasonication process was performed at a frequency of 0.5 kHz with an inlet ultrasound power of around 1 W/mL (UIP 1000hd ultrasonic processor, Hielscher ultrasound technology) for about 15 min. After ultrasonication of nanoparticulate silver in acrylic component of 100% PU coating, the dispersion was placed in vacuum oven at 50 °C for 2 h to remove ethanol which was included in nanoparticulate silver dispersion. A stoichiometric ratio of polyisocyanate to polyol is considered for 100% polyurethane coatings; however, for the waterborne coating polyisocyanate was added 50% excess to the stoichiometry according to the manufacturer recommendation. The high solid polyurethane and waterborne polyurethane coatings containing 0, 100, 200, 300 ppm nanoparticulate silver were denoted as HPU0, HPU100, HPU200, and HPU300 and WPU0, WPU100, WPU200 and WPU300, respectively.

2.3. Procedure and sample preparation for EIS measurements

The mild steel panels with a dimension of 200 mm × 10 mm × 0.8 mm were used as the metal substrate. For surface cleansing, all substrates were firstly abraded by 600 and 800 grit sandpaper. Then, the abraded panels were, degreased in acetone, and left to dry at room temperature. The coatings were applied on clean mild steel panels with film applicator (BYK Gardner).

Coatings were allowed to cure for 1 week at room temperature. After curing, the coatings with dry film thickness of 30 ± 2 μm were chosen for EIS measurements. EIS was measured on three replications. The EIS measurements were carried out in a three electrode system by Ivium Compactstat. Silver–silver chloride (3 M KCl) electrode and graphite rod were used as a reference electrode and auxiliary electrode, respectively. An area of 1 cm^2 of the coated panels with the above-mentioned thickness was considered to be exposed to 3.5% NaCl solution, and the rest areas of the panels were sealed with a beeswax–colophony mixture. The EIS was measured in the frequency range of 10 kHz to 0.01 Hz, with 10 mV perturbation (peak to zero) at open circuit potential.

Electrochemical impedance spectra were obtained from the coated samples after 10, 24, 40, 70 and 100 days of immersion in 3.5% NaCl solution. Ivium Equivalent Circuit Evaluator software was used for determining the equivalent circuit.

2.4. Procedure and sample preparation for SEM

As the same way for preparation of the coatings for the EIS measurements, the coatings containing 0 and 200 ppm nanoparticulate silver were prepared and applied on glass substrate. The cross-section of coatings was examined before immersion and after 100 days immersion in NaCl solution by scanning electron microscopy (SEM), Leo 1455 VP. The cross section of the coatings was studied under 21,000× magnification.

2.5. FTIR spectroscopy

FTIR spectra of polyurethane coatings were recorded by Perkin-Elmer Spectrum One spectrometer, using KBr pellets. The measurements were carried out in the range of 450–4000 cm^{-1}.

3. Results and discussion

3.1. EIS measurement

Electrochemical impedance spectra obtained from the HPU and WPU coated samples after 10, 24, 40, 70 and 100 days of immersion in 3.5% NaCl solution are shown in Figs. 1 and 2, respectively. It should be noted that the noisy points were eliminated from the spectra. Almost all samples show a reduction of impedance magnitude at low frequencies during immersion time. Such a diminution could be attributed to water diffusion through the coatings. HPU coatings show one time constant spectra during 100 days of immersion, while second time constant appears for WPU200 and WPU300 coatings after 24 and 70 days, respectively. The first time constant is related to the coating film, while appearance of second time constant could be related to the corrosion beneath the coating.

According to Figs. 1 and 2, phase angle at 10 kHz is around −90° for HPU coatings during immersion period, while it becomes more positive for nanoparticulate silver incorporated WPU coatings during immersion. When the phase angle at high frequencies is around −90° it means that current tends to pass through the coating capacitance, which results in capacitive behavior of the coating [26]. Correspondingly, current pass through the coating resistance leads to positive shift for phase angle at high frequencies, which results in resistive behavior of the coating [26]. It seems that the presence of nanoparticulate silver in WPU coating results in formation of conductive pathways and consequently more resistive behavior of the coatings.

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