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Mechanical and anticorrosion properties of nanosilica-filled epoxy-resin composite coatings

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ABSTRACT

Homogeneous, 50-μm-thick, epoxy coatings and composite epoxy coatings containing 2 wt% of 130-nm silica particles were successfully synthetized on austenitic stainless steel of the type AISI 316L. The surface morphology and mechanical properties of these coatings were compared and characterized using a profilometer, defining the average surface roughness and the Vickers hardness, respectively. The effects of incorporating the silica particles on the surface characteristics and the corrosion resistance of the epoxy-coated steel were additionally investigated with contact-angle measurements as well as by potentiodynamic polarization and electrochemical impedance spectroscopy in a 3.5 wt% NaCl solution. The silica particles were found to significantly improve the microstructure of the coating matrix, which was reflected in an increased hardness, increased surface roughness and induced hydrophobicity. Finally, the silica/epoxy coating was proven to serve as a successful barrier in a chloride-ion-rich environment with an enhanced anticorrosive performance, which was confirmed by the reduced corrosion rate and the increased coating resistance due to zigzagging of the diffusion path available to the ionic species.

1. Introduction

The total cost and environmental consequences of corrosion problems have become a major challenge to engineers [1]. Austenitic (AISI) stainless steel is known as an important engineering material, due to its generally high corrosion resistance combined with favourable mechanical properties, such as its high tensile strength [2,3]. The high corrosion resistance of this stainless steel is attributed to the presence of a passive film, which is stable, invisible, thin, durable and extremely adherent and self-repairing [4]. However, in many aggressive environments, such as a chloride-ion-rich environment, AISI is still observed to suffer from pitting corrosion [5]. Therefore, in the past two decades, the modification of metallic surfaces by various coatings, organic or polymeric, has become part of an important procedure in enhancing particular surface properties, such as scratch resistance, oxidation and corrosion.

Epoxy resin is one of the most common polymer matrixes that are widely used to protect steel reinforcements in concrete structures [6,7] because of its excellent mechanical properties, chemical resistance, good electrical insulating properties and strong adhesion to heterogeneous substrates. Epoxy coatings not only reduce the corrosion of a metallic substrate by providing an effective physical barrier between the metal and the environment containing an aggressive species, such as an enhanced chloride-ion concentration, O_2 or H^+, they also serve as a reservoir for corrosion inhibitors that help the steel surface to resist attack from aggressive species.

However, in spite of a successful application, pure epoxy coatings are often susceptible to damage by surface abrasion and wear [8] and show poor resistance to the initiation and propagation of cracks due to a highly cross-linked structure [9]. Therefore, many efforts have been made by researchers to improve the properties of epoxy by adding various nanofillers [10–18]. They studied the favourable effects of particle size, volume fraction and the quality of the dispersion on the mechanical response of the polymer composites [11,19–23]. In addition, a lot of attention has been paid to epoxy coatings containing nanoparticles that show a significantly improved barrier performance for corrosion protection by decreasing the porosity and zigzagging the diffusion path for the deleterious species [24].

This work investigates the influence of silica nanoparticles on the surface morphology, mechanical characteristics and anticorrosion behaviour of composite epoxy coatings. We focus on the direct incorporation of a low percentage of silica nanoparticles

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into the epoxy matrix, expecting a dramatic improvement in the examined characteristics.

2. Experimental

2.1. Materials

Epoxy resin (Epikote 828LVEL, Momentive Specialty Chemicals B.V.) was mixed with a hardener 1,2-Diaminocyclohexane (Dytek DCH-99, Invista Nederland B.V.) in the ratio 100:15.2 wt% and used as the matrix in the composite. Composite reinforcing silica (SiO_2) nanoparticles with a mean diameter of 130 nm were synthesized following the Stöber–Fink–Bohn method [25]. Diglycidyl ether of bisphenol A (Sigma-Aldrich) was used as the silica surface modifier to prevent agglomeration. Imidazole (Sigma-Aldrich) served as a reaction catalyst.

Austenitic stainless steel AISI 316L (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) was used as a substrate.

2.2. Surface modification of silica

Silica and diglycidyl ether of bisphenol A (modifying agent) were mixed in the ratio 40:100 wt% and dispersed in 50 mL of toluene in the presence of imidazole (25 wt%). The mixture was then refluxed at 100 °C for 2 h. To remove the by-product (imidazole) it was centrifuged three times using acetone as a solvent. The remaining silica was then dispersed in acetone and stirred at room temperature for 2–3 h. Finally, the acetone was removed and the silica was dried in an oven at 110 °C for a few hours.

2.3. Steel substrate preparation

The steel sheet with a thickness of 1.5 mm was cut into plates of 15 mm in width and 75 mm in length for the mechanical testing and into discs of 15 mm diameter for the electrochemical examination. Prior to the application of the coating the steel plates and discs were prepared by a mechanical procedure, initially ground with SiC emery paper down to 1200 grit, and then rinsed with distilled water.

2.4. Composite coating preparation

Epoxy-based composites were prepared by blending with 2 wt% of 130-nm surface-modified SiO_2 particles. To improve the dispersion of the silica particles in the coating, they were dispersed in epoxy resin using a solvent. Acetone was used as a solvent, since the Fourier-transform infrared spectroscopy (FTIR) and FT-Raman analysis [26] indicated that the processing in acetone did not chemically alter the epoxy network. Prior to the addition of the silica particles, both the resin and the hardener were separately diluted in acetone with a 1:1 weight ratio. The nanoparticles were then dispersed in the epoxy resin/acetone solution using ultrasonification for 20–30 min at room temperature. After adding the hardener/acetone solution in the next step, the mixture was manually stirred for a few minutes. Finally, 10–20 μl of the silica/epoxy resin/hardener/acetone mixture was poured onto the steel substrate plates and a uniform film was then applied to the substrate using a wet film applicator. The prepared coatings were degassed under vacuum for 10–15 min to additionally remove the excess solvent. The composite coating was then cured in two steps. The composite coatings were first pre-cured at 70 °C for 1 h and then post-cured at 150 °C for another hour. The resulting coatings on the steel-substrate plates were 50 μm thick. For comparison, neat epoxy coatings without silica fillers were also prepared and cured in the same process as the composites.

2.5. Vickers hardness test

The Vickers hardness measurements were performed using a FV-700 Future-Tech corp. device. The hardness values were measured immediately after the indentation with a 0.5 kg load for 15 s. The fracture-toughness values were calculated accordingly. Photomicrographs of the morphology of the indents were taken using a Nikon optical microscope.

2.6. Surface roughness

A profilometer, model Form Talysurf Series 2 (Taylor-Hobson Ltd.), was employed for the surface analysis. The instrument has a lateral resolution of 1 μm and a vertical resolution of about 5 nm. It measures the surface profile in one direction. The topography of the surface was acquired by combining several measurements in parallel directions that were 2 μm apart. The samples were measured with a 1 mm^2 spot size.

TalyMap gold 4.1 software was used for both the image processing and the roughness analysis. The software offers the possibility to calculate the average surface roughness, S_a, for each sample, based on the general surface roughness equation (Eq. (1)):

$$S_a = \frac{1}{L_x}\frac{1}{L_y}\int_0^{L_x}\int_0^{L_y} \left|z(x, y)\right| dxdy, \tag{1}$$

where L_x and L_y are the acquisition lengths of the surface in the x and y directions and $z(x,y)$ is the height. To level the profile, corrections were made to exclude the general geometrical shape and possible measurement-induced misfits.

2.7. Contact-angle measurements

The static contact-angle measurements of water (W) and glycerol (G) on a clean AISI 316L sample ground with SiC emery paper down to 1200 grit and on the pure epoxy and silica/epoxy composite coatings prepared on an AISI 316L steel substrate were performed using a CAM200 (KSV Nima) contact-angle goniometer. Liquid drops of 5 μl were deposited on different spots of the substrates to avoid the influence of roughness and gravity on the shape of the drop. The drop contour was analysed from the image of the deposited liquid drop on the surface and the contact angle was determined by using Young–Laplace fitting. To minimize the errors due to roughness and heterogeneity, the average values of the contact angles of the drop were calculated approximately 80 seconds after the deposition from at least five measurements on the studied coated steel. All the contact-angle measurements were carried out at 20 °C and ambient humidity. As contact angles were only available for two polar liquids, an equation-of-state approach [27] was used to calculate the corresponding surface energies.

2.8. Potentiodynamic measurements

Potentiodynamic measurements were performed on the AISI 316L stainless steel, ground with SiC emery paper down to 1200 grit and on the AISI 316L stainless-steel substrate coated with epoxy and silica/epoxy composite coatings in a 3.5 wt% NaCl solution (Merck, Darmstadt, Germany). The specimens were embedded in a Princeton Applied Research (PAR) Teflon holder and employed as the working electrode (WE). The reference electrode (RE) was a saturated calomel electrode (SCE, 0.242 V vs. SHE) and the counter