



Polyaniline-clay composite-containing epoxy coating with enhanced corrosion protection and mechanical properties

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ABSTRACT

The corrosion of steel is a worldwide industrial problem. In this study, we demonstrate that polyaniline (PANI), an extensively studied additive for organic coatings that affords corrosion protection, can be imbedded in epoxy, as a pigment in a clay composite, to protect steel against corrosion. The PANI-clay composite was synthesized in situ by oxidative polymerization and the coating was formulated by dispersing PANI-clay composite particles were dissolved in (N-methyl pyrrolidone) NMP by ultra-sonication and then mixed into an epoxy resin using a wooden spatula. The addition of low levels of clay improved the BET (Brunauer-Emmett-Teller) surface area of PANI. Improved corrosion protection was observed through immersion testing and electrochemical studies; 33.4% of the surface of the neat epoxy coating was covered in rust, while only 19.3% of the epoxy composite surface was covered. Furthermore, electrochemical studies showed that the corrosion rate was reduced by the incorporation of the PANI-clay composite particles in epoxy resin, which exhibited a protection efficiency of 76.2%. The composite-containing epoxy film also exhibited superior mechanical properties. Therefore, the enhanced performance of the epoxy-based composite coating material makes it suitable for a wide range of applications.

1. Introduction

Steel and iron are the most extensively used metals in our industrialized society; however they are prone to corrosion, which is a worldwide problem that impacts industry enormously [1]. Corrosion is a chemical reaction in which corrosive species, such as oxygen, water vapor and salts deteriorate a metal. The corrosion problem is more prominent where steel is exposed to the atmosphere, and preventative methods have largely provided unsatisfactory results. Such methods include the galvanization of metals with zinc, the pretreatment of steel by phosphating, the use of chromium-containing compounds (CCCs), and cathodic protection (Cp). However, each of the currently applied solutions has associated problems. The acidity of rain influences the zinc corrosion rate in outdoor environments for metallic coatings [2]. Phosphating processes are labor-intensive and the work environment is hazardous [3]. Cps result in poor adhesion properties and CCCs are associated with environmental and health concerns [4]. The many disadvantages associated with current coating systems have led to the development of organic coatings.

An organic coating is a modified film that forms a protective barrier between the environment and the substrate. However, defects in the

coating layer provide pathways by which corrosive species can reach the metal surface. Hu et al. [5] reported that, without pre-treatment, organic coatings are poor adhesive, and achieving a uniform film devoid of defects is difficult. Modifying the coating with intrinsically conducting polymers (ICPs) can result in improved films.

ICPs have been used in the coatings industry because of their electrochemical and conducting properties [6,7]. They are also used in the electronics industry [8], in energy-conversion systems, such as solar cells [9], in antistatic coatings, light emitting diodes [10], and sensors [11]. The unique properties of polyaniline (PANI), which include its ease of synthesis, low synthesis cost, and tunable conducting properties compared to other ICPs [12], have attracted the most interest. While the chemical and electrical properties of ICPs are good, they tend to have poor mechanical strengths; however their mechanical properties can be improved through the incorporation of inorganic clays such as montmorillonite (MMT) in the polymer [13]. MMT is a phyllosilicate clay mineral that is formed by stacked layers of aluminum octahedrons and silicon tetrahedrons [14], and MMT have already been used in ICPs to improve their properties [15].

Other researchers have shown that organic composite coatings have superior electrochemical and anticorrosive properties [16–19]. Adams

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and colleagues [20] used a PANI/clay composite as a primer and reported that the anticorrosive properties of PANI/clay on iron samples were better than those of pure PANI. Substantial research has been conducted on PANI as an anticorrosion additive, but there are few reports on PANI as a pigment. Pigments can also be used as corrosion-protection additives, for film reinforcement, and to improve coverage and adhesion properties. In this study PANI and a PANI/MMT composite are used as pigments and incorporated into epoxy resin. The corrosion-protection efficiency and the mechanical properties of the coated films are investigated electrochemically and by immersion testing.

2. Experimental

2.1. Materials

Hydrochloric acid (HCl) and acetone were obtained from Minema Chemicals, South Africa. Aniline, ammonium persulfate (APS), and N-methylpyrrolidone (NMP) were purchased from Sigma Aldrich, South Africa. Bisphenol-A epoxy resin and the polyamide-based curing agent were obtained from Advanced Laboratory Solutions, South Africa. MMT was obtained from Ecce Holdings, Pty. Ltd., South Africa. All materials were used as received.

2.2. Synthesis of PANI

A monomer solution containing 20 mL of HCl (3 M) and 1.8 mL of 1 M aniline was premixed in a 500 mL jacketed flask connected to a circulating bath at a temperature of -7°C . The oxidant solution was prepared by dissolving 0.6 g of APS in 20 mL of 3 M HCl in a 50 mL beaker and cooled to -7°C in a freezer. The oxidant solution was added dropwise to the monomer solution and the reaction was stirred for 4 h at -7°C . The solution was decanted into a 100 mL beaker and stored at 4°C for 10 h. The precipitate was collected by centrifugation, rinsed with HCl (3 M) and acetone, and finally dried at room temperature for 36 h.

2.3. Synthesis of the PANI-MMT composite

The PANI-MMT composite was synthesized using the in-situ chemical oxidative polymerization technique described above for the polymerization of pristine PANI, with the exception that MMT was dispersed at loadings of 3, 5, 10, and 20% (w/w) into the aniline/HCl solution, in a 500 mL jacketed flask and stirred until the temperature of the dispersion was -7°C (30 min). The monomer was polymerized with the oxidant solution at -7°C with stirring for 4 h, as described above. The solution was decanted into a 100 mL beaker and stored at 4°C for 10 h. The precipitate was collected by centrifugation, rinsed with HCl (3 M) and acetone, and finally dried at room temperature for 36 h.

2.4. Coating formulation and application

The epoxy resin and the curing agent were not modified prior to use. The PANI composite, prepared as described above, was dispersed in 5 mL of NMP with varying the amount from 0.05 to 0.2 g. The dispersed composite in NMP was ultra-sonicated at 23°C for 10 min and then mixed with 10 mL of the resin using a wooden spatula. The curing agent (hardener) was added to the mixture of the resin and the composite at an epoxy:hardener ratio of 100:13.5 (v/v). The panels (1-mm-thick steel substrates that were either 8×16 cm or 5×5 cm in size) were cut from a steel-sheet using Laser-cutter and were sand blasted and rinsed with acetone and left to air-dry. Finally, the coatings were applied by levelling method at room temperature to panels.

2.5. Characterization

The thermomechanical properties of PANI and the composites were measured by dynamic mechanical analysis (DMA, DMA800, Perkin Elmer, USA) using a powder cell in dual cantilever-bending mode. The temperature dependences of the storage flexural modulus (E'), loss modulus (E''), and $\tan \delta$ (E''/E') of neat PANI and the composites were measured at a heating rate of $2^{\circ}\text{C}/\text{min}$ and a constant frequency of 1.0 rad/s in the $-100 - 100^{\circ}\text{C}$ temperature range.

The BET surface areas and pore sizes were determined using a Micromeritics TRISTAR 3000 surface-area analyzer using the low-temperature N_2 -adsorption method. Prior to analysis, each sample was degassed at 70°C for 4 h under a continuous flow of N_2 gas to remove volatile moisture and adsorbed contaminants. Field-emission scanning electron microscopy (FESEM) was carried out using a Zeiss Auriba microscope (Zeiss, Germany) operating at 3 kV. Samples were sputter-coated with carbon to avoid charging prior to imaging. The structure and properties of the PANI and the clay nanocomposite were investigated using the PANalytical XPERT-PRO (the Netherlands) X-ray diffractometer (XRD) using Ni filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a fixed slit at 45 kV (voltage) and 40 mA (current) in the 2θ diffraction angle range of $0^{\circ} - 40^{\circ}$. In order to determine the corrosion resistances of the films, immersion testing was carried out in a 3.5 wt% NaCl solution for 30 days according to international standard ASTM G31. The panels were weighed prior to immersion in the electrolyte solution to evaluate weight loss. The degree of rusting was analyzed according to international standard ASTM D610-01 for steel substrates. An Autolab potentiostat/galvanostat (PGSTAT302 A) three-electrode cell was used for electrochemical analyses. An Ag/AgCl electrode was used as the reference electrode, the coated steel was the working electrode, and a platinum electrode was used as the counter electrode, in a 3.5% NaCl electrolyte solution. Linear polymerization was determined at a starting potential of -0.5 V and a stop potential of 1.5 V ; the step potential was 0.048 V and the scan rate was $0.002 \text{ V}/\text{sec}$. The electrical conductivity of the composite was measured using a system that was specifically designed by us for measuring the electrical properties of powder materials (more detailed can be found in Appendix A). The resistivities of the compacted powders were calculated on the basis of the measured resistances in the conduction region. The conductivity of the coated steel was measured using a Keithley 4200 SCS Semiconductor Characterization System in current- and voltage-sweep modes, from -5 to 5 V , and with a hold time of 0.01 s at room temperature using a two-point probe. The adhesion strength (pull-off test) was measured using an Instron 5966 tester according to EN ISO 4624 standard.

3. Results and discussion

3.1. Surface morphologies and structural analysis

The SEM morphologies of the various samples in this study are shown in Fig. 1, which reveals that the MMT has a stacked-sheet-like structure Fig. 1(A), while PANI has a fibrous structure Fig. 1(B). The SEM image of the 3 wt. % MMT-containing composite presented in Fig. 1(C) exhibits a greater proportion of the fibrous structure with few compacted regions that are ascribable to clay agglomeration or fibers that form mats. The 5 wt. % MMT-containing composite exhibits a more compact structure, with less of the fibrous PANI structure observed, Fig. 1(D). Sapurina et al. [21] reported that the fibers formed during the polymerization of PANI form two dimensional structures that are referred to as “micro mats”; these woven articles produce mats composed of several layers of fibers, which is consistent with the compact structures observed in the 3 and 5 wt.% MMT-containing composites. The high BET surface areas listed in Table 1 could also be ascribable to these mats. The SEM image of the 10 wt. % MMT-containing composite shown in Fig. 1(E) exhibits fibrous structures on the MMT surface,

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