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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Anticorrosive Performance of New Epoxy-Amine Coatings Based on Zinc Phosphate Tetrahydrate as a Nontoxic Pigment for Carbon Steel in NaCl Medium

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Abstract
Epoxy resin is known to react with a hardener such as polyamine to form a thermoset 3D polymer net with an outstanding physical and mechanical properties. They are widely used in coating and adhesives. In this study, we present a new epoxy resin material useful for making an anticorrosive formulation for carbon steel. The epoxy resin presented in this study is diglycidyl ether 4,4′-dihydroxy diphenyl sulfone (DGEDDS). It was prepared in a two-step process that involves reacting epichlorohydrin with 4, 4′ dihydroxy diphenyl sulfone then with sodium hydroxide. The structural elucidation of DGEDDS was carried out with Fourier transform infrared. The anticorrosive formulation DGEDDS–MDA–ZPH was prepared from DGEDDS and the hardener 4,4′-methylene dianiline (MDA) in the presence of the anticorrosion pigment zinc phosphate tetrahydrate (ZPH). Another standard formulation (DGEDDS–MDA) was prepared without ZPH. The physicochemical and anticorrosive performance of the coated carbon steel was evaluated using electrochemical impedance spectroscopy (EIS). The coated surface was subjected to morphological characterization by SEM before and after immersion in the corrosive medium and exposing it to the UV radiation. The value of the polarization resistance (R_p) obtained by the EIS method for the standard coating DGEDDS–MDA and epoxy composite coating DGEDDS–MDA–ZPH was 31898 and 72611 $\Omega\,cm^2$ during the 1 h of immersion in 3 wt% NaCl, respectively. After aging by exposing the coatings for a 2000 h to UV radiation the values were dropped to 2596 and 5189 $\Omega\,cm^2$, respectively. The values show the high stability and resistance of the epoxy resin coating to electrolytes and UV radiation. The coating even showed higher stability in the presence of ZPH pigment. As shown in the results, the tricomponent composite showed an outstanding stability in protecting carbon steel form corrosion in an aggressive marine environment where UV is very intense and the humidity and salts are very high.

Keywords Epoxy resin · Zinc phosphate tetrahydrate · Coating · Carbon steel and electrolyte

1 Introduction

It is well known that steel must be protected from oxidation and exposure to electrolyte due to corrosion. Various methods have been developed for such purpose. Some examples include inorganic-based coating. However, one major issue with these methods is that, the inorganic-based coatings are unable to form a film on metals simply by coating and then drying.

One solution to this issue is the use of the organic-based anticorrosion coating. Recently organic-based coatings are becoming more important as they are easy to apply on the metal surface and very effective in protecting steel from cor-

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rosion. Organic-based coatings showed usefulness in many industries such as aeronautics, automobiles, ships and oil tanks [1–3]. Among the organic coating, epoxy resin-based protective coatings received the highest attention due to its outstanding mechanical properties, high thermal stability, good chemical resistance, good corrosion resistance and could be produced at low cost [4,5].

Organic coating forms physical barrier between the metal surface and the corrosive environment, thus preventing the electrolytes from diffusing to the metal interface [6]. However, with the time and under sever conditions of UV radiation and presence of electrolytes the coating resistance starts to fail and microcracks develop on the surface. The electrolyte thus penetrates the coating matrix through these microcracks to the metal surface. Causing the adhesion between the coating and the metal surface to become weak. One way of increasing the stability and the resistance to damage of the organic formulation is adding to it an inorganic pigment [7]. Zinc chromate is one of the anticorrosive pigments most used in the epoxy resins formulations. Unfortunately, the carcinogenic and toxic nature of the zinc chromate pigment has limited its use. Currently there is great interest in a new generation of anticorrosive pigments with high efficiency and environmental friendly to replace the toxic pigments in the anticorrosive formulations [8,9].

The toxicity and possible carcinogenicity of the current formulations have motivated us to offer a new a nontoxic one for metal protection in aggressive marine-corrosive environment.

The coating formulation is a combination of the epoxy resin diglycidyl ether 4,4′-dihydroxy diphenyl sulfone (DGEDDS, the curing agent 4,4′-methylene dianiline (MDA) and the nontoxic anticorrosion pigment zinc phosphate tetrahydrate (ZPH).The combination of these three materials produced a steel coating that can endure aggressive marine environment where UV is very intense and the humidity and salts are high [10].

2 Experimental

2.1 Materials and Methods

All materials and solvents include 4,4′-sulfonyl diphenol, epichlorohydrin, sodium hydroxide, ethanol, 4,4′-methylene dianiline, zinc phosphate tetrahydrate were purchased from Aldrich chemical company and use without any further purification.

2.2 Synthesis of Diglycidyl Ether 4, 4′-Dihydroxy Diphenyl Sulfone (DGEDDS)

In a three-necked, fitted with a condenser and a dropping funnel, was placed 2.5 g of 4, 4′ dihydroxy diphenyl sulfone (10^{-2} mol) and 8.25 g of sodium hydroxide (10 wt%). The mixture was heated to 60 C for 10 minutes with stirring, then 4.32 g of epichlorohydrin was added. The temperature of the reaction mixture was raised to a 100 °C in 20 minutes and maintained for at this temperature about for 3 h.

The reaction mixture was then cooled down to room temperature and transferred to a separatory funnel. The aqueous layer was removed and organic layer was dissolved in chloroform and washed several times with distilled water dried over sodium sulfate. Solvent and excess epichlorohydrin were removed under reduced pressure using rotary evaporator. The residue was a brown viscous resin (89% yield). The structure of the produced epoxy was verified by FT-IR using a Bruker Fourier transform infrared (FT-IR) equipped with a attenuated total reflection technique.

2.3 Epoxy Coating Application

Two coating formulations were prepared by mixing a stoichiometric amount of MDA hardener and epoxy resin (DGEDDS) without and with zinc phosphate tetrahydrate pigment (5 wt%). Ethanol was added as a diluent. The two formulations were applied on the surface of carbon steel by a film applicator. The steel substrates were abraded with sand papers of 600, 800 and 1200 grades followed by ethanol degreasing. Coated steel samples were cured in an oven under vacuum at 70 °C for 4 h to complete curing and removal of solvent. The dry thickness of the coatings on the steel surface after curing was about 170 ± 10 µm. A schematic diagram epoxy formulation preparation is shown in Fig. 1.

2.4 Coating Evaluation Under Accelerated Conditions

Coating evaluation under aging conditions was carried out by exposing the coated specimens to UV light. A commercial UV-A lamps (center wavelength 340 nm) was used this purpose. The amp produces a UV radiation power with a density of 50 mW/cm^2. The aging temperature was regulated at 30 °C in the presence of oxygen. All samples were exposed to UV radiation for 2000 h with a geometric area of 1 cm^2.

2.5 Electrochemical Impedance Spectroscopy Analysis

Corrosion protection performance of samples was evaluated using an electrochemical impedance spectroscopy (EIS) analysis at the frequency range of 100 kHz–10 mHz and an AC amplitude of 10 mV using Potentiostat PS 200. The electrochemical measurements were performed in 3 wt% NaCl solution using a classical three-electrode setup. The three electrodes were a reference electrode a saturated calomel electrode (SCE), platinum ring counter electrode (CE) and the working electrode (WE) which is a piece cut from the coated carbon steel samples with 1 cm^2 area.