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Water-based & eco-friendly epoxy-silane hybrid coating for enhanced corrosion protection & adhesion on galvanized steel

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ABSTRACT

In this current study, epoxy-silane hybrid coatings were designed to investigate their anti-corrosion performance and adhesion on galvanized steel. Silanes with alkoxy group, epoxy group, amine group and thiol group were chosen to understand the role of functionalities in the performance of designed hybrid coatings. Moreover, the silanes were added at three different concentrations into epoxy polymer to asses the effect of concentration on anti-corrosion and adhesion properties of the coating films. From scanning electron microscopic (SEM) images, we observed a uniform coating without any agglomeration of coating particles over galvanized steel substrates. The corrosion performance of casted and cured films was evaluated by using potentiodynamic polarization and AC impedance spectroscopy method. The physical properties, such as, thermal behavior and thermo-mechanical behavior were studied using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) respectively. The adhesion strength between coating films and galvanized steel substrate was checked by 'pull off' adhesion test.

It was found that due to the grafting of sol-gel coatings onto organic polymer backbone, the adhesion property and anti-corrosive performance has improved remarkably as compared to non-grafted epoxy polymer. It was observed that amino silane showed superior performance compared to thiol silane. The poor performance of thiol silane grafted epoxy coating could be attributed to some chemical incompatibility of hydrophobic and non-polar sulfur silane moiety and hydrophilic and polar water-borne epoxy polymer backbone. Addition of silane by 1 wt% and 3 wt% into epoxy polymer backbone caused improvement in both anti corrosive property and adhesion strength but further increase of the silane concentration to 5 wt% led to deterioration of protective property of the films. This drop in performance can be attributed to excessive consumption of epoxide groups in epoxy resin by amino and thiol functionalities present in silane.

1. Introduction

In past few years, inorganic-organic hybrid films have been used to improve the performance of anti-corrosive coating on different metal substrates [1–3]. Extensive study on silane chemistry is still being carried out to improve performance of such coatings to protect metal substrate against corrosion [4–7]. Organofunctional silanes are silane based chemicals bearing organic as well as inorganic moieties in a single molecule [8]. The general structure is given as $(RO)_3SiY$, where —OR is a hydrolysable alkoxy group and Y is organofunctional group, such as, peripheral epoxy group, active amine group, thiol group etc [9,10]. One of the distinguishing features of silane compounds is that even a small amount of silane can offer major enhancement of the adhesion between polymeric matrices and the metal surface. In general, the silanes need to be hydrolyzed in dilute aqueous solution prior to application [8,10]. However these thin films of silanes are too brittle and cannot provide long term protection. Initially they act as physical barrier towards permeation of water and corrosive ions [11]. But once saturated with electrolyte solution, the silane films lose their barrier property and the metal oxide/hydroxide at coating-metal interface starts playing a critical role in corrosion protection [11–13]. So, it is not advisable to use only silane films to achieve effective long-term protection against corrosion due to their very low thickness.

Epoxy resins are widely used in protective coating, adhesive and encapsulating material due to their strong chemical resistance,

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adhesion and good processing characteristics. However, the epoxy resin cannot provide satisfactory result in humid condition due to its hydrophilic nature [14,15]. The high water uptake tendency of epoxy resins restricts its application [14]. Hence, to overcome the problems associated with silane film and epoxy film, researchers have explored the improved performance of hydrolyzed silane modified epoxy films in past decades. This kind of epoxy-silane hybrid leads to remarkable improvement of adhesion as well as anti-corrosive characteristic due to the fact that higher Si-O bond energy promotes strong adhesion and organic polymer backbone offers additional improvement of barrier property of thin silane film and formation of crack free three-dimensional network [14].

The current work involved designing of epoxy-silane hybrid coatings to investigate their anti-corrosion performance and adhesion on galvanized steel. Silanes with alkoxy group, epoxy group, amine group and thiol group were used to modify epoxy polymer to explore the role of functionalities in the performance of designed hybrid coatings. The silanes were added at three different concentrations (1 wt%, 3 wt% and 5 wt%) into epoxy coating to assess the effect of concentration on anti-corrosion and adhesion properties of the coating films.

It was found that due to the grafting of sol-gel coatings onto organic polymer backbone, the adhesion property and anti-corrosive performance did improve remarkably as compared to non-grafted epoxy polymer alone. Also, silane concentration of 1 wt% and 3 wt% in epoxy polymer backbone led to improvement in both anti corrosive property and adhesion strength. Further increase of silane concentration to 5 wt% led to deterioration of the protective property of the films. This drop in performance can be attributed to excessive consumption of epoxide groups in epoxy resin through crosslinking reaction with amino and thiol functionalities present in silane. Moreover, it was observed that amino silane showed superior performance compared to thiol silane. The poor performance of thiol silane grafted epoxy coating could be attributed to some chemical incompatibility of hydrophobic and non-polar sulfur silane moiety and hydrophilic and polar water-borne epoxy polymer backbone.

Additionally, these coatings do have benefits of low VOC and are free from toxic and carcinogenic elements which are the basic requirements of a coating for compliance with safety, health and environmental regulations.

2. Experimental

2.1. Synthesis of sol-gel coating and sol-gel grafted epoxy resin

In our present study, we formulated three types of sol-gel coating solutions by hydrolysis and condensation of silane molecules with aid of water.

a) The reference coating solution was formulated by hydrolyzing glycidoxy-propyl tri ethoxy silane (GPTS) and methyl tri ethoxy silane (MTEO) in 1:1 molar ratio (Coating I) using acetic acid as catalyst.
b) Phenyl-amino-propyl tri ethoxy silane (PAPTS) was added to reference coating solution by1 wt% and was named as Coating II.
c) Mercapto-propyl-triethoxy silane (MPTS) was added to reference coating solution by1 wt% to form Coating III.
d) The water based epoxy polymer was Bisphenol-A-(epicholorohydrin) type and the curing agent for epoxy resin was polyamide based. Both epoxy polymer and the curing agent were kindly provided by Berger Paints India Ltd. The mass ratio of epoxy resin to polyamide was 10/8. The mixture of epoxy and polyamide was diluted by DI water in 1:1 ratio by weight.

Table 1
Composition of epoxy-silane hybrid coating and their nomenclature.

Formulation	Name
Epoxy polymer + Coating I (1wt%)	Hybrid IA
Epoxy polymer + Coating II (1wt%)	Hybrid IIA
Epoxy polymer + Coating III (1wt%)	Hybrid III A
Epoxy polymer + Coating I (3wt%)	Hybrid IB
Epoxy polymer + Coating II (3wt%)	Hybrid IIB
Epoxy polymer + Coating III (3wt%)	Hybrid IIIB
Epoxy polymer + Coating I (5wt%)	Hybrid IC
Epoxy polymer + Coating II (5wt%)	Hybrid IIC
Epoxy polymer + Coating III (5 wt%)	Hybrid IIIC

The detail procedure of preparation of three types of sol-gel coatings (Coating I, Coating II and Coating III) has been described elsewhere [16]. The sol-gel solutions were added to mixture of epoxy and polyamide resin at 1 wt% (Hybrid A), 3 wt% (Hybrid B) and 5 wt% (Hybrid C) respectively. At the end we obtained nine sets of formulation. The formulations and their nomenclature have been tabulated in Table 1.

2.2. Sample preparation, coating application and heat treatment

Galvanized sheets of dimension 4 cm × 6 cm were used as test piece for the investigation. These samples were cleaned with 8% (w/v) aqueous sodium silicate alkali solution and dried prior to coating application. The cleanliness of the surface was checked by water breaking test ensuring that there was no oil/grease left on the surface. Coating solutions were applied on the surface with Apex Spin NXG-P1 spin coater with different speeds for 2 min to obtain smooth and uniform film. The coated samples were cured at room temperature for twelve hours and heated in a hot air oven at a temperature of 100 °C for 5 min to ensure complete curing [17]. With the controlled coating technique, it was possible to achieve a final dry film thickness of 10 ± 5 μm as measured by DFT meter, Positest DFT-Combo Model Ferrous & non ferrous, Defelsko, USA.

2.3. Characterization

Fourier Transform IR spectroscopy was used to characterize the structure of cured epoxy coating and sol-gel grafted epoxy coating. All infrared spectra were recorded on a Nicolet 670 FTIR spectrometer. One drop of solution of each coating was placed on KBr window for the FTIR analysis. The thermal behavior of the coatings was investigated by differential scanning calorimetric method (DSC) and was conducted on TGA Q500 Universal TA Instrument (U.K) at temperature range of 25 °C to 100 °C at a heating rate of 10 °C/min. The viscoelastic property of pure epoxy and hybrid films was studied by using a DMTA IV instrument (Rheometric Scientific, USA) in tensile mode in the temperature range of 30 °C to 200 °C at a heating rate of 10 °C/min. The surface morphology of the coated substrates was observed under FESEM using S4300 SEIN HITACHI Japan at 10 kV. Before analysis, the samples were gold sputtered to suppress the charging effect. The corrosion analysis of bare and coated samples was performed with Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) technique. The data were obtained using an Autolab instrument constituting frequency analyzer, potentiostat and Nova software (1.10.1.9). All the electrochemical tests were performed in 3.5 wt%NaCl solution. Edges of each sample were sealed with waterproof tape to prevent premature corrosion along the edges of the panels [28]. A typical three