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Synthesis and characterization of a unique isocyanate silane reduced graphene oxide nanosheets; Screening the role of multifunctional nanosheets on the adhesion and corrosion protection performance of an amido-amine cured epoxy composite

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ABSTRACT

The present study focuses on improving the adhesion bonding strength between an amido-amine cured epoxy coating and steel substrate and decreasing the cathodic delamination rate via a new surface pre-treatment method through decoration of steel/epoxy interface by graphene oxide (fGO) nanosheets covalently functionalized with 3-(Triethoxysilyl) propylisocyanate. The effect of fGO film on the organic coating behavior was determined by electrochemical impedance spectroscopy, Pull-off adhesion, water contact angle, cathodic delamination and salt spray tests. It was found that steel surface pre-treatment by fGO coatings could remarkably improve the adhesion strength and corrosion prortection properties and reduce cathodic delamination rate.

1. Introduction

Organic coatings, by creating a physical barrier between the metal surface and the corrosive electrolyte, provide one of the most applicable and effective protection approaches of metallic structures against corrosion damages in many industries. The adhesion loss as well as cathodic disbonding is considered as an important failure mechanism for the organic coatings applied on the metallic structures which occurs at the coating/metal interface, leading to direct contact of bare metal to the corrosive electrolyte [1,2]. In fact, these coatings are permeable to corrosive agents such as water, oxygen and corrosive ions (i.e. Cl^- and Na^+). The electrolyte passes through the coating porosities and reaches the metal surface, resulting in the increase of pH at the coating/metal interface as a result of oxygen reduction reaction producing hydroxyl ions on the cathodic regions. Production of corrosion products and strong alkaline environment at the metal/coating interface results in the adhesion loss and coating delamination and therefore the coating corrosion protection performance decreases significantly [3–9].

One strategy for obtaining long-term protection of metal structures against corrosion is improvement of adhesion properties of the organic coatings on the substrates [10]. One of the factors which weakens the adhesion strength between the sub-layer and the subsequent organic coating is the presence of various contaminants such as rust, oil, salts and metal oxide and hydroxide on the surface of substrate [11]. Physical and/or chemical removal of these contaminants is essential before application of coating to achieve stronger interfacial adhesion bonding between the organic coating and the metal substrate. In this regard, different surface preparation methods including chemical treatment by acid, alkaline cleaning, conversion coatings and silane based treatments have been proposed [12–14]. The chemical treatment by conversion coatings (such as chromate and phosphate based coatings) result in significant improvement of the interfacial adhesion bonding through changing the chemistry, increasing the surface free energy, and the physics, increasing the roughness, of the substrate. Because of the presence of micro cracks and porosities in the phosphate coatings, these coatings are sealed using dilute chromic acid solution. However, the use of chromates is strictly forbidden due to its toxic nature and bad effects on the human health [15,16]. So attemptes

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have been performed to find a suitable environmenltally friendly approaches for chemical treatment of steel surface. In this regard, silane pre-treatment has been proposed as an eco-friendly method in recent years. But these coatings have low thickness and high permeability and therefore does not show good corrosion resistance [17,18].

Newly, many researches have focused on functionalized of graphene oxide in order to increase the corrosion resistance and adhesion properties of the organic coating to the metallic substrates. Graphene oxide (GO) contains many functional groups (hydroxyl, carbonyl and carboxyl groups on the edge and epoxide groups on the basal plane of GO nanosheets) and these groups are suitable reactive sites for chemical modification of GO nanosheets. Covalent functionalization of graphene oxide by new reactive groups (for example amine, isocyanate, epoxy, or alkyl groups) is an effective method for improving the interfacial interaction between the polymer and GO nanosheets [19–22].

Recently, many researchers have focused on prevention of metallic substrates against corrosion through application of graphene layers [20,23–29]. Also the graphene based materials have been used as efficient filler in polymer matrix composites [9,19,21,22,30–38]. Kang et al. [23] improved the oxidation resistance of iron and copper foils through deposition of reduced graphene oxide multilayer coating. Raman et al. [27] developed a graphene coating on the copper substrate by chemical vapor deposition (CVD) method for protecting it from electrochemical degradation. Also, Kirkland et al. [28] studied the corrosion resistance of the graphene coating on the copper and nickel substrate in aqueous electrolyte. Park and Park [39] established electrophoretic deposition of graphene oxide on mild steel and studied its anti-corrosion properties. The results showed that the GO coating did not provide enough protection for the substrate because this coating has not sufficient density, and the coating porosities act as the corrosion initiation sites. Aneja et al. [40] created (3-Aminopropyl)triethoxysilane (APTES) functionalized graphene coatings on the steel substrates as an anti-corrosive alternative to chromate (VI) based systems and showed that the performance of this new coating is better than that of chromate based coatings. Tong et al. [20] studied the corrosion and wear resistances of a graphene oxide coating on the surface of silanized Mg–Zn–Ca alloy. They showed that the silane/GO duplex coating remarkably improve the anti-corrosion properties of Mg alloy owing to its stable chemical bondings (through amidation reaction) and blocking the permeation of chloride ions toward the surface of Mg substrate. In addition, they showed that the GO coating enhances the wear resistance and reduces the friction coefficient of the substrate. Xue et al. [29] reported the preparation of protective graphene-based film on AA2024-T3 aluminum alloy surface through immersion in a solution containing 3-glycidoxypropyl-trimethoxysilane functionalized graphene oxide solution and indicated that the silane-GO coating has effective adhesion strength and corrosion protective properties. Ramezanzadeh et al. [36] created amino functionalized graphene oxide (FGO)/epoxy composite coating on the mild steel substrate for enhancement of barrier and corrosion protection performance of the epoxy coating. The results showed that incorporation of FGO nanosheets into the epoxy coating significantly increased the corrosion resistance of the coating through improving its barrier properties and also ionic resistance. In another work, Ramezanzadeh et al. [41] studied the effect of APTES functionalized GO nanosheets filler in silane coating (mixture of tetraethylorthosilicate (TEOS) and APTES) on the steel plates and showed that this composite film could significantly increase the corrosion protection performance and decrease the cathodic delamination rate of the epoxy organic coating upon the steel plates.

In this work, we aim to introduce a new surface pretreatment method of steel utilizing 3-(Triethoxysilyl)propylisocyanate (TEPI) functionalized graphene oxide (fGO) thin film coating and its effect on the adhesion bonding strength and cathodic disbonding properties of the epoxy coating. Covalent functionalization of GO by TEPI silane was considered to provide strong covalent bonds between the fGO thin film and epoxy organic coating and on the other hand increase the work of adhesion and the surface free energy of the steel substrate. This improves the adhesion strength between the steel substrate and epoxy organic coating. For this purpose, after covalent functionalization of GO nanosheets by TEPI, the fGO thin film coating was created by dipping the steel substrate in ethanol and DMF baths comprising fGO nanosheets. Then the epoxy organic coating was applied on the pre-treated and untreated steel specimens. The functionalized GO nanosheets were characterized by Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). The fGO thin film created on the steel surface was evaluated by X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and contact angle measurements. Also electrochemical impedance spectroscopy (EIS), salt spray, pull-off and cathodic delamination tests were used to study the effect of fGO thin film on the epoxy organic coating properties.

2. Experimental

2.1. Materials

For synthesis of the graphene oxide, the expandable graphite powder with carbon content of 98–99.5%, grain size of 80% > 300 μm and expansion rate of 350–700 cm^3/g was prepared from Kropfmuehl Graphite Co. (Germany). Other materials i.e. H_2SO_4 (98%), $KMnO_4$ and H_2O_2 (30%) were prepared from Aldrich Co. (Germany). 3-(Triethoxysilyl)propyl isocyanate (TEPI, $(C_2H_5O)_3Si(CH_2)_3NCO$) was purchased from Aldrich Co. (Germany). Ethanol (C_2H_5OH, 96%) and N,N-dimethyl formamide (DMF) were prepared from Hamoon Co. (Iran) and Merck Co., respectively. Sodioum hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Mojallali Co. (Iran). Epoxy resin (Araldite GZ7 7071 × 75) and amido polyamide curing agent (CRAYAMID 115) were prepared from Saman Co. and Arkema Co., respectively. The epoxy value, solid content and density of the epoxy resin were 0.1492–0.1666 Eq/100 g, 74–76% and 1.08 g/cm^3, respectively. The solid content, viscosity and density at 40 °C of the hardener were 50%, 50,000 cps and 0.97 g/cm^3, respectively. The steel panels (0.04 wt% Al, 0.05 wt% P, 0.05 wt% S, 0.34 wt% Si, 0.32 wt% Mn, 0.19 wt% C and 99.01 wt% Fe) with dimensions of 90 × 80 × 2 mm were prepared from Foolad Mobarakeh Co, Iran.

2.2. Synthesis and covalent functionalization of GO by TEPI

Graphene oxide (GO) nanosheets was prepared through a modified Hummer's method [32]. In a typical experiment, the graphite powder (0.5 g) was added to H_2SO_4 (60 mL) under constant stirring for one hour. Then $KMnO_4$ powder (1.5 g) was gradually added to the solution (while the temperature was kept at less than 20 °C by using of an ice water bath) and the resulting mixture was stirred for 12 h at ambient temperature. After that, the distilled water (600 mL) was added to the mixture under vigorous stirring. Then, the suspension was further oxidation treated with 30% H_2O_2 solution (5 mL). At the end, the mixture was centrifuged and washed by 1 M hydrochloric acid (two times) and deionized water (three times), respectively. Finally, an aqueous solution of GO nanosheets was obtained.

The covalent functionalization of GO nanosheets by TEPI silane was carried out in DMF solvent. For this purpose, briefly, 50 mg