Distinctive roles of silane coupling agents on the corrosion inhibition performance of graphene oxide in epoxy coatings

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ABSTRACT

Although graphene oxide (GO) is an unique 2D material for improving the corrosion resistance of polymeric coatings, GO nanosheets easily form aggregates in polymer matrix which provide obstacles in front of achieving high protective coatings. The main goal of this research is to enhance the corrosion inhibiting performance of GO nanofiller in epoxy coatings via modifying the surface of GO sheets with silane coupling agents. We have employed 3-aminopropyl triethoxysilane (APTES) and 3-glysidyloxypropyl trimethoxysilane (GPTMS) as silane agents with amine and epoxy end-groups, respectively, to investigate the effect of silane type on the properties of nanocomposite coatings. The results reveal that silane functionalization of GO significantly improves the adhesion of coatings on metal substrate and increases the water contact angle on epoxy coatings. Although all the prepared nanocomposites show superior barrier properties via tortuousing the diffusion path of corrosive species in epoxy matrix, electrochemical analysis exhibit that incorporation of APTES-GO with amine end-groups more efficiently enhances the corrosion resistance of epoxy coating. The investigation offers new aspects for selecting the kind of silane agent for modifying GO sheets and developing epoxy coatings with high corrosion protection efficiency.

1. Introduction

Corrosion of metallic structures is one of the most serious challenges of nearly every industry [1–3]. Extending the service life of the existing structures has a great importance to achieve the multi-goal of improving corrosion resistance, decreasing financial costs, and increasing safety at work [3,4]. In this regard, organic coatings are generally used to protect metallic structures against corrosion [5,6]. It is generally assumed that these polymeric coatings play as a physical barrier between metal substrate and corrosive environment [7].

Meanwhile, solvent based-epoxy coatings are widely used as commercial coatings in aggressive environments; because they show properties such as excellent adhesion to metals, excellent chemical resistance, outstanding processability, and low cost [8–11]. Despite that, epoxy coatings contain hydrophilic hydroxyl groups in their cured network; leading to their poor resistance in humidity conditions due to hydrolytic degradation [12,13]. Besides, initiation and propagation of cracks happens in epoxy coatings during exposure to corrosive electrolyte [10]. Therefore, corroding agents including water, oxygen and destructive ions like Cl^- and H^+ can permeate through the defects into

the coating and reach at the metal/coating interface; thus reducing the coating adhesion and enhancing the corrosion of the metallic substrate beneath the coating [14,15].

Consequently, extensive studies have been directed on improving the corrosion protection efficiency and barrier properties of epoxy coatings [16,17]. Recent researches show that graphene oxide (GO) as a two dimensional nanofiller of sp^2-hybridized carbon atoms, remarkably improves the corrosion resistance of polymeric coatings via increasing the diffusion path of corrosive agents as well as decreasing coating porosity [18–21]. However, to ensure effective dispersion of GO in polymer coatings and strengthening the interfacial bonding between GO and polymer matrix, surface modified GO is an alternative choice to prevent GO agglomeration and improve corrosion resistance of coating [22–24].

GO has oxygen containing groups such as hydroxyl, carboxyl, and epoxy groups on its basal plane and edges which provide reactive sites for covalent fuctionalization [18,24]. Amongst different covalent functionalization methods considered for GO dispersion in polymer matrix [7,19,25–27], silane modification of GO is a promising method for improving the properties of the composites [22–24]. The alkoxy

groups of silane coupling agent and the hydroxyl groups of GO take part in a chemical reaction and after that, the remained functional groups of silane molecules on GO sheets provide chemical bonding between GO and polymer matrix [22,24]. On the other hand, organo-functionalized silanes have been used directly in epoxy coatings for improving corrosion resistance of coatings due to formation of dense –Si–O– bonds within epoxy organic chains [28–32]. Thus, it can be assumed that the performance of epoxy coatings would be comprehensively enhanced via utilizing the advantages of silane functionalized GO (f-GO).

In this regard, Wan et al. [22] used 3-glycidoxypropyltrimethoxy silane (GPTMS) to functionalize GO and their results pointed out that the compatibility between the functionalized GO and the epoxy matrix improved and therefore, storage modulus, glass transition temperature, thermal stability, tensile and flexural properties, and fracture toughness of epoxy composites promoted. Also, Wang et al. [33] used 3-amino-propyltriethoxysilane (APTES) to covalently functionalize graphene sheets. Their study showed that functionalization of graphene sheets with silane agent is an appropriate approach for achieving high interfacial interactions between graphene sheets with epoxy matrix even at a high nanofiller loading (1 wt.%); hence, thermal stability, tensile strength and elongation to failure of epoxy composites improved. In addition, Li et al. [34] studied the mechanical properties of silane functionalized GO-epoxy nanocomposites. In this research, they used two differently terminated silane coupling agents including APTES and GPTMS. While nanocomposites containing amino-functionalized GO (APETS-GO) showed more significant increase in Young's modulus and tensile strength, nanocomposites containing epoxy-functionalized GO (GPTMS-GO) revealed more increase in ductility and fracture toughness.

All the above mentioned investigations have focused on mechanical and thermal properties of epoxy nanocomposites containing f-GO. From the corrosion resistance point of view, Sun et al. [35] used encapsulated reduced graphene oxide (rGO) with APTES as high aspect ratio nanofiller in polyvinyl butyral coating. Their results showed that the barrier properties of the coating have improved. Also, Mo et al. [18] compared the effect of GO and APTES-GO on corrosion resistance of polyurethane coatings and they found that GO dispersion in polymer matrix improves by silane modification, leading to enhanced tribological and anti-corrosion properties of polyurethane composite coatings.

Therefore, the main aim of this research is to investigate the effect of GO modification with different silane coupling agents on corrosion protection performance of solvent-based epoxy coatings. In this work, we have considered the effect of GO functionalization with two different silane coupling agents including APTES and GPTMS on properties of epoxy coatings. Further, the corrosion resistance of nanocomposite coatings was considered via electrochemical methods and salt spray test to evaluate the impact of silane type on corrosion protection efficiency of epoxy coating.

2. Experimental

2.1. Materials

Natural graphite flakes (< 20 μm) were purchased from Sigma–Aldrich. All chemical regents used for GO synthesis including potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4), H_2O_2, and HCl were all analytical grade from Merck. Silane coupling agents including (3-aminopropyl) triethoxysilane (APTES, 99%) and (3-glysidyloxypropyl) trimethoxysilane (GPTMS, ≥98%) were obtained from Merck. Diglycidyl ether of bisphenol A epoxy resin (Epon 1001, epoxy equivalent mass = 480–550, Shell Resin Co.) and polyamide hardener (Versamid 115, amine value = 230–246 mg KOH/g) were used to prepare epoxy coatings. The solid content of epoxy resin and hardener are 75% and 50%, respectively. Mild carbon steel plates (ST-12) were purchased from Foolad Mobarakeh Co. of Iran. Mild steel panels were sandblasted and then, they were degreased with acetone before coating.

2.2. Synthesis of GO

GO was synthesized according to modified Hummers method [36–38]. 1 g natural graphite powder was added into 50 mL concentrated H_2SO_4 and the mixture was stirred for 2 h at ice bath. Then, 6 g $KMnO_4$ was added very slowly to the suspension and the reaction temperature was kept below 15 °C. Subsequently, the mixture was stirred at 35 °C for 24 h until pasty brownish product was obtained. It is then diluted with slow addition of deionized (DI) water and the oxidation reaction was terminated by pouring H_2O_2 solution. For purification, the mixture was washed by HCl and DI water several times to remove residual acids and salts. The graphite oxide was subsequently suspended in DI water and exfoliated by high-energy sonication (Probe Sonicator, Misonix-S400) to yield GO. Finally, the GO was dried at 50 °C.

2.3. Synthesis of silane-functionalized GO

Two different silane coupling agents including APTES and GPTMS were used to prepare silane functionalized GO (f-GO); the prepared f-GO samples are abbreviated as A-GO and G-GO, respectively. In order to prepare f-GO samples, 20 mg GO was dispersed in 40 mL DI water via bath sonicator (Elmasonic-P 120H) for 60 min. Then, 5 mL of 0.2 M toluene solution containing silane precursor was added to the prepared GO solution. The obtained brownish solution was refluxed with continuous stirring at 70–80 °C for 24 h. The resulting f-GO with dark brown color was washed with ethanol and DI water and dried at 50 °C [39].

2.4. Preparation of nanocomposite coatings

Epoxy nanocomposite coatings containing 0.1 wt.% f-GO were prepared as follow: First of all, f-GO powder was probe sonicated (Misonix-S400) for 1 h in an organic solvent. Then it was added into the predetermined amount of polyamide hardener, followed by 5 min sonication. After preparing a homogeneous dispersion of f-GO in polyamide hardener, it was stirred and heated at 70 °C to evaporate the solvent. Next, the prepared mixture was added to the stoichiometric amount of epoxy resin at room temperature. It should be mentioned that the stoichiometric mixing ratio for epoxy resin and hardener are 1:1 by weight. The prepared mixture was mixed with a mechanical mixer for 15 min. Subsequently, the prepared nanocomposites were placed in vacuum oven for 1 h to degas and then, applied by air spray on sandblasted mild steel substrates which were cleaned by acetone and blow-dried. The coated substrates were cured at room temperature and post-cured at 90 °C for 1 h. The thickness of coatings was in the range of 150 ± 10 μm.

In order to compare the effect of f-GO on corrosion resistance of epoxy coatings, pure epoxy coatings and epoxy nanocomposite coatings containing GO were prepared. Pure epoxy coatings were prepared via mechanical mixing epoxy resin and hardener in stoichiometric amount. Epoxy/GO nanocomposites containing 0.1 wt.% GO were obtained by the same procedure mentioned for epoxy/f-GO nanocomposite coatings. It should be mentioned that, in this research, nanofillers were added directly to polyamide hardener due to its lower viscosity compared to epoxy resin in order to obtain good dispersion of nanofillers in polymer matrix; since our previous studies have shown that the dispersion of GO in low viscosity polymer matrix is better than that with high viscosity [40].

2.5. Characterizations

Crystalline structure of GO and f-GO powders were studies by X-ray diffraction technique (XRD, Philips PW 3710, 30 kV, 35 mA, Cu Kα) and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum-GX) over wavelength range of 500–4000 cm^{-1}. The mor-