Surface & Coatings Technology 317 (2017) 1–9

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Excellent corrosion protection performance of epoxy composite coatings filled with amino-silane functionalized graphene oxide

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ARTICLE INFO

Article history:
Received 20 December 2016
Revised 16 March 2017
Accepted in revised form 21 March 2017
Available online 22 March 2017

Keywords:
Epoxy
Amino-Silane
Graphene oxide
Nanocomposite coating
Corrosion protection

ABSTRACT

Epoxy coatings containing graphene oxide (GO) and amino-silane modified GO (A-GO) with various weight fractions (0.05, 0.1, 0.3, and 0.5 wt%) are prepared to investigate the effect of silane modified GO on performance of nanocomposite coatings. (3-Aminopropyl) triethoxysilane (APTES) is used as organosilane for A-GO synthesis. A-GO is characterized by FTIR, XRD, FE-SEM, and EDS. The dispersion quality of nanosheets in epoxy coating is examined by FE-SEM, revealing the interfacial interaction of GO in coating has improved via silane modification. Besides, the pull-off adhesion strength of epoxy coating to substrate increases by about two times via adding A-GO. The results of electrochemical impedance spectroscopy show that epoxy/A-GO coatings can provide superior corrosion protection performance and maximum corrosion resistance is achieved via adding 0.1 wt% A-GO. By increasing the loading of A-GO, the barrier properties decrease due to agglomeration of nanosheets in polymer matrix.

1. Introduction

Corrosion is an inevitable gradual destruction of metallic structures and has major impacts on economics of industrial nations [1]. Various strategies have been developed to control the corrosion phenomenon [2] and meanwhile, organic coatings are considered as one of the most promising methods to protect metals against corrosion [1,3]. In this regard, epoxy resins are widely employed as coatings due to their stable chemical properties, excellent corrosion resistance, outstanding adhesion, low curing shrinkage, high tensile strength, and flexural strength [4,5]. However, these epoxy resins are inherently brittle and micropores are inevitably produced in their structure due to solvent evaporation [5,6].

Meanwhile, nanomaterials are a favorable option for overcoming the shortcomings of traditional organic coatings and developing advanced coatings with longer service life [7]. Graphene oxide (GO) nanosheets, which consist of quasi-two-dimensional honeycomb lattice of carbon atoms with hydroxyl and epoxide functional groups on basal planes and carbonyl and carboxyl groups on the edges [7,8], have attracted considerable attention of researchers; due to their outstanding inherent properties including sheet-like structure, high specific surface area, electrical insulation, superior mechanical strength, and barrier properties against oxygen, water and corrosive ions [4,9–11].

However, GO nanosheets tend to agglomerate within polymer matrix as a result of high surface area and strong Van der Waals interaction [6]. In order to solve this problem, the most convenient strategy to prepare high performance composites is chemical modification of GO sheets [12]. In this regard, covalent and non-covalent modifications of GO nanosheets are promising methods to improve the interfacial interactions of nanofillers in polymer matrix [13]. For example, Wan et al. [14] used diglycidyl ether of bisphenol-A (DGEBA) for modifying GO nanosheets and they found that GO nanosheets grafted with DGEBA show better dispersion quality in epoxy matrix compared to unmodified GO, providing enhanced thermal and mechanical properties for epoxy composites. Tang et al. [11] used triglycidyl para-aminophenol (TGPAP) as surface modifier on GO sheets and they reported that the dispersion and exfoliation of GO nanosheets in epoxy matrix remarkably improves via GO modification with TGPAP, leading to improved mechanical properties. Ramezanzadeh et al. [15] prepared functionalized GO by using aromatic diamine *p*-phenylenediamine (PPDA) to improve the interaction of GO with epoxy matrix and enhance the corrosion protection performance of epoxy coatings on mild steel substrates. Qi et al. [16] prepared GO sheets grafted with thermotropic liquid crystalline epoxy (TLCP) to enhance the thermal and mechanical properties of epoxy composites.

Moreover, organosilane coupling agents have been used for modifying the surface of GO nanosheets. In this regard, Li et al. [17] used amino- and epoxy-functionalized GO through a wash-and-rebuild process via two different silane coupling agents including (3-aminopropyl)

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http://dx.doi.org/10.1016/j.surfcoat.2017.03.050
0257-8972/

trimethoxysilane (APTMS) and (3-glycidoxypropyl) trimethoxysilane (GPTMS), respectively. They found that APTMS-GO and GPTMS-GO have different reinforcing effect upon the mechanical properties of epoxy composites; epoxy composites containing APTMS-GO yielded higher Young's modulus and tensile strength, while epoxy composites containing GPTMS-GO show higher increase in ductility. Wan et al. [18] studied the effect of unmodified GO and silane functionalized GO (GPTMS-GO) on the mechanical properties of epoxy composites; their findings confirmed that the improved mechanical properties of epoxy composites is due to covalent bonding between silane modified GO and epoxy matrix which enhances the dispersion and interfacial interactions in the polymer matrix. Wang et al. [19] used (3-aminopropyl) triethoxysilane (APTES) for chemically grafting GO sheets in order to homogeneously disperse GO in epoxy matrix. Their results show that the prepared nanocomposites show higher thermal stability, tensile strength, and elongation to failure.

As mentioned above, although the effect of silane functionalized GO nanosheets on mechanical and thermal properties of epoxy coatings have been investigated, to the best of our knowledge, there is not a comprehensive study on their corrosion protection performance. In our previous study [20], we have used tetraethyl orthosilicate (TEOS) as silane coupling agent for in-situ decoration of SiO_2 nanoparticles on GO sheets and the results showed that the corrosion resistance of epoxy/SiO_2-GO nanocomposite coatings is significantly higher than epoxy/GO samples. In order to investigate more precisely the effect of silane coupling agents on modification of GO nanosheets for application in epoxy coatings, functionalization of GO sheets with APTES (A-GO) is considered in this research. It should be mentioned that APTES is selected as silane coupling agent due to its amine-end groups in order to enhance the compatibility between functional groups of GO sheets with polymer matrix [18]; because A-GO and/or GO sheets are directly added to polyamide hardener with low viscosity (compared to epoxy resin with high viscosity) in order to enhance their dispersion quality in polymer matrix [21–24]. Indeed, amine-end groups of A-GO nanosheets are compatible with amine groups of polyamide hardener, leading to better distribution of A-GO sheets in coating matrix.

In this research, GO and A-GO with different weight percentages are dispersed in polymer matrix to prepare epoxy/GO and epoxy/A-GO nanocomposite coatings via curing process on mild steel substrates. The dispersion quality of nanofillers in polymer matrix, the pull-off adhesion strength, and the corrosion protection properties of the prepared nanocomposite coatings are investigated. The main aim of this research is to utilize the advantages of both GO nanosheets and amino-silanes for enhancing the corrosion protection performance of epoxy coatings.

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. (3-Aminopropyl) triethoxysilane (APTES, 99%, Merck) is used as amino-silane coupling agent. 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) with chemical composition presented in Table 1 were purchased from Foolad Mobarakeh Co. of Iran. Mild steel panels were sandblasted and then, they were degreased with acetone before using as substrate for coatings.

Table 1
Chemical composition (wt%) of mild carbon steel (ST-12).

Element	Fe	Si	C	S	P	Mn	Al
Wt%	Balance	<0.1	0.1	<0.025	<0.025	0.5	0.07

2.2. Preparation of amino-silane functionalized GO

GO was prepared from pristine graphite powder according to modified Hummers method [25]. Then, APTES was grafted on GO sheets via a facile route. In a typical procedure, 20 mg GO was dispersed in 40 mL DI water by using 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 amino-silane functionalized GO (A-GO) with dark brown color was washed with ethanol and DI water and dried at 50 °C [26].

2.3. Preparation of nanocomposite coatings

Nanocomposite epoxy coatings containing different loadings (0.05, 0.1, 0.3, and 0.5 wt%) of as-prepared GO and A-GO sheets were prepared by the following procedure. First, sheets were dispersed in acetone by sonication for 1 h at room temperature. Then, the prepared solution was mixed with polyamide hardener, followed by sonication for 10 min to achieve a homogeneous black suspension. Subsequently, it was heated at 50 °C while stirring to evaporate the solvent. Next, the prepared mixture was mixed with stoichiometric amount of epoxy resin (resin to hardener weight ratio of 1:1) by using high-shear mechanical mixer. The prepared nanocomposites were placed in vacuum oven to degas for 1 h and 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 for 1 week and post-cured at 90 °C for 1 h. The thickness of coatings was in the range of 150 ± 10 μm. Moreover, pure epoxy coating as reference coating was prepared via mechanically mixing epoxy resin and polyamide hardener in stoichiometric amounts.

2.4. Characterizations

X-ray diffraction technique (XRD, Philips PW 3710, 30 kV, 35 mA, CuKα) was performed on GO and A-GO nanosheets. Fourier transforms infrared spectra (FTIR, Perkin Elmer Spectrum-GX) of GO and A-GO sheets were obtained over wavelength range of 400–4000 cm^{-1}. The morphology of GO and A-GO powders was considered by field emission scanning electron microscopy (FE-SEM, MIRA3 TESCAN). Energy dispersive X-ray spectroscopy (EDS) was carried out accompanied by FE-SEM to evaluate the elemental analysis of the prepared A-GO powder. The dispersion quality of GO and A-GO samples in coating matrix was observed by FE-SEM (MIRA3 TESCAN). Adhesion strength of coatings to mild steel substrate was measured by pull-off method (Positest pull off, Defelsko, USA) according to ASTM D4541-09 and the reported pull-off data are the average of 3 different measurements on the surface of coatings.

2.5. Corrosion tests

The electrochemical behavior and corrosion protection performance of pure epoxy, epoxy/GO, and epoxy/A-GO samples were studied by electrochemical impedance spectroscopy (EIS) on an Autolab (potentiostat/galvanostat, PGSTAT 30). In this configuration, a three electrode cell including coated mild steel substrate as working electrode, a platinum rod as counter electrode, and saturated calomel electrode (SCE) as reference electrode was employed. The electrochemical measurements were carried out at open circuit potential (OCP) in 3.5 wt% NaCl aqueous solution. EIS tests were recorded in frequency range of 10^{-2} to 10^5 Hz utilizing AC amplitude of 10 mV. The obtained electrochemical data were analyzed with the help of Nova 1.8 software.