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Corrosion-resistant hybrid coatings based on graphene oxide–zirconia dioxide/epoxy system

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ABSTRACT

The hybrid coatings based on graphene oxide–zirconia dioxide/epoxy (GO–ZrO_2/EP) system were fabricated and applied for corrosion protection of metal substrate. First, GO–ZrO_2 hybrid was synthesized through two different silane coupling agents and the morphology and structure were confirmed by Field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis. Then, GO–ZrO_2 was incorporated into EP to investigate the corrosion protection of metal substrate. Investigations revealed that the corrosion protective properties were significantly enhanced by the addition of GO–ZrO_2 to EP. The enhancement attributed to the sheet-like structure, uniform dispersion and exfoliation of GO–ZrO_2 hybrid within EP matrix, which effectively prevented the underlying metal substrate from corrosion attack.

1. Introduction

Corrosion, an increasingly serious issue, is the deterioration of metal by chemical interaction with their surrounding environment, which would cause substantial damage to society and industry all over the world [1,2]. To address this issue, several methods for the protection of metal substrates have attracted huge attention in recent decades, such as cathodic protection, anodic protection, corrosion inhibitors, coating, and alloying [3,4]. Among the various approaches, polymer coatings are regarded as most effective method to prevent metals from corrosion.

Epoxy resins (EP), the conventional coating, are widely used as polymeric coatings, composite matrix, adhesives, and structural materials due to their anticorrosion properties, chemical stability, low shrinkage, excellent adhesion, thermal stability, and electrical resistance [5–7]. Unfortunately, EP also has some undesirable properties, such as brittleness, poor flexibility and impact resistance [8], resulting in plentiful tiny pores easily produced when fabricating the high temperature curing epoxy solvent-borne coatings, which may attenuate their barrier properties. As a result, many researchers tend to toughen EP by means of nanofillers, thermoplastics or rubbers [9,10]. Amongst various toughening methods inclusion of nanoparticles into EP is a common way to provide a durable protection for substrate due to their high specific surface area, small size, functionality and cost-effective preparation [10–12].

Graphene oxide (GO) is one of the most important graphene derivatives, which consists of oxygenous groups such as hydroxyl, carboxylic and epoxide groups on their basal planes and edges [13–15]. Polymers containing GO have spurred intense interest in industries due to its intriguing properties. However, GO sheets are prone to form severe aggregations within polymer, arising from their intrinsic van der Waals' interaction and huge specific surface area [16–18], which caused poor distribution of GO within EP and limited their further application. The abundant oxygen functional groups existed in the surface of GO, which made it easily functionalized with organic components. Ramezanzadeh et al. successfully functionalized GO with an aromatic diamine [19] and aliphatic polyisocyanate [20], and the functionalized GO sheets achieved excellent dispersion within epoxy/polyurethane matrix and the corrosion protection properties of corresponding coatings were reinforced. Qian et al. [21] asserted GO was functionalized with amine-terminated polyether and then incorporated into polyurea matrix, which improved the dispersion of GO in the polymer matrix and enhanced the thermal stability, mechanical properties of composites coatings. Qi et al. [22] demonstrated that grafting

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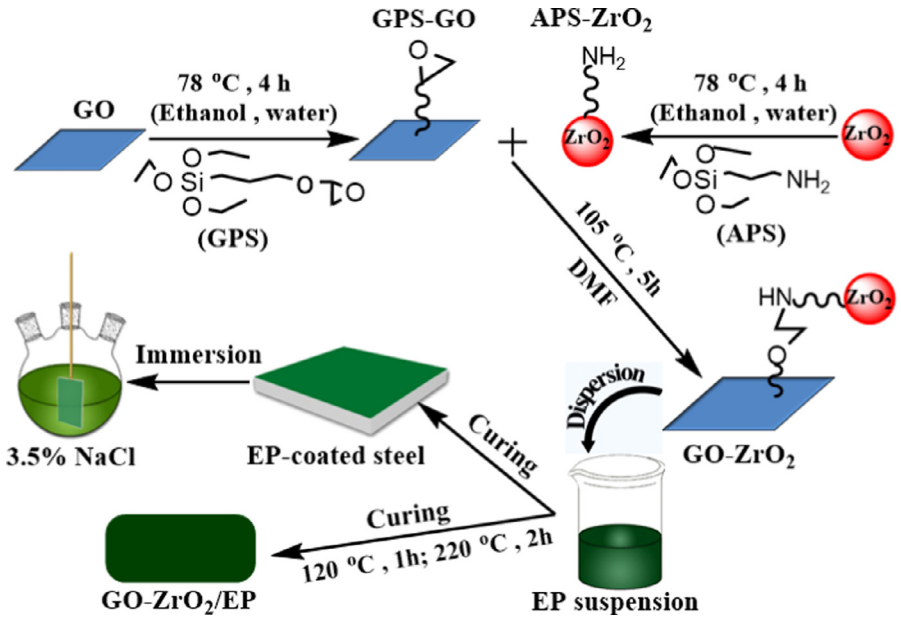

Fig. 1. Schematic of preparation of GO–ZrO_2 and the corresponding hybrid coatings.

polymethylmethacrylate (PMMA) on GO exhibited synergistic properties of building blocks and hereby prevented corrosion from the copper substrate. Li et al. [23,24] reported amino/epoxy-functionalized GO were fabricated utilizing two different silane coupling agents, they found amino/epoxy-functionalized GO exhibited better distribution within EP and the mechanical properties of composite coatings were enhanced. Lee et al. [25] investigated GO nanosheets were functionalized with different silane coupling agents and then introduced into EP coating, and they showed proper dispersion in the matrix and strengthened interfacial bonds of the carbon/epoxy composites. Wan et al. [26] functionalized GO with 3-glycidoxypropyltrimethoxysilane (GPS) (silane-f-GO). The results showed improved compatibility and dispersion between the sheet and the epoxy matrix, thus leading to increase of the mechanical properties of epoxy composites. Recently, some studies reported GO was decorated with nanoparticles and improved its properties, such as titanium oxide [27], zinc oxide [28], and silica [29]. However, relatively few studies involved in fabricating GO–ZrO_2 hybrid in the presence of different silane coupling agents and then dispersing hybrid in polymer to investigate the corrosion protective performance of composite coatings. Particularly, nanostructured structure of ZrO_2, as one of most promising materials employed in polymeric coatings [30], which exhibited excellent chemical resistance, wear resistance and corrosion resistance, high hardness, strength and fracture toughness, providing a good opportunity for a large number of industrial application [31–33]. In addition, ZrO_2 nanoparticles were incorporated to polymer, which was environmentally acceptable owing to the nontoxicity of inherent nanoparticles. There was the report involved functionalized ZrO_2 with 3-aminopropyltrimethoxysilane (APS) dramatically enhanced the corrosion resistance of EP coating [30]. Based on mentioned above, amino functionalized ZrO_2 (APS–ZrO_2) and epoxy functionalized GO (GPS–GO) were synthesized by different silane coupling agents: APS and GPS, respectively, then GPS–GO was decorated with APS–ZrO_2 to obtain GO–ZrO_2 hybrids, which not only combined their inherent advantages, but obtained loose structured GO and improved the dispersion of nanoparticles within polymer.

In the present work, GO–ZrO_2 hybrid was fabricated through the reaction between APS–ZrO_2 and GPS–GO. Afterwards, GO–ZrO_2 hybrid was incorporated into EP to prepare the composite coating, and the dispersion of hybrid within EP matrix was demonstrated by the FE-SEM, EDS mapping and XRD analysis. The corrosion protection of composite coatings was investigated by electrochemical measurements (Nyquist, Bode and Tafel plots), coatings' morphology monitoring and EDS analysis. Investigations indicated that incorporation of GO–ZrO_2 into EP significantly enhanced the corrosion protective properties of EP composite coatings. In addition, the schematic of preparation of GO–ZrO_2 and the corresponding hybrid coatings was shown in Fig. 1.

2. Experimental

2.1. Materials

The following materials used in the experiment were purchased from Chengdu Kelong Chemical Reagent Factory (China): natural graphite powder, 98% concentrated sulfuric acid (H_2SO_4), 30% hydrogen peroxide (H_2O_2), 37% hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), *N*, *N*-dimethylformamide (DMF), anhydrous ethanol (analytical reagent grade), sodium chloride (NaCl), and silane coupling agents (SCA): APS, GPS. Nanostructured ZrO_2 was provided by Beijing Deke Daojin Science And Technology Co., Ltd. The EP emulsion (modified WSP-6101) AT-1 and its curing agent its hardener PN-1 (density: 1.17, epoxide value: 0.12, solid content: 65 wt%) used in this research were supplied by Bluestar Technology Wuxi Resin Factory and Chengdu Shida Strength Shield Technology Co., Ltd. (Local company in Chengdu, China), respectively. Deionized water (DI water) was produced by a water purification machine (UPC-III-40 L, Ulupure).

2.2. Preparation of GPS–GO

GO was fabricated via a modified Hummers' method [34,35], then functionalized by GPS to increase the amount of epoxy groups. Briefly, 0.05 g of GO and 1 g of GPS were dispersed in 50 g of anhydrous ethanol by ultrasonication to form a homogenous solution, followed by stirring at 78 °C for 4 h. Then, 5 g of distilled water was added dropwise into the mixture. Finally, the solution

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