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RGO modified ZnAl-LDH as epoxy nanostructure filler: A novel synthetic approach to anticorrosive waterborne coating

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ABSTRACT

The reduced graphene oxide zinc aluminum layered double hydroxides (rGO-ZnAl-LDH) micro-nano fillers were prepared via a one-step process, then modified by 3-aminopropyl triethoxysilane and incorporated into a water-borne epoxy (EP) matrix to produce M-rGO-ZnAl-LDH/EP composite coating. The effects of the M-rGO-ZnAl-LDH hybrid on the corrosion resistance of the coating were studied by adjusting the ratio of GO: ZnAl-LDH and also the adding amount of M-rGO-ZnAl-LDH hybrid. The anticorrosive nature of the M-rGO-ZnAl-LDH/EP composite coating had been investigated by potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and salt spray test. The results indicated that the corrosion resistance of the coating was improved remarkably when the ratio of GO: ZnAl-LDH was 2:1 and the adding amount was 0.5 wt% into EP. The corrosion current density (i_{corr}) was only 0.0733 μA/cm^2 and the coating resistance (R_c) was up to 2.77E4 Ω cm^2 for M-rGO-ZnAl-LDH/EP (2:1–0.5 wt%), while the i_{corr} for pure EP was 0.469 μA/cm^2 and the R_c for pure EP was 2.10E3 Ω cm^2, which suggested that the M-rGO-ZnAl-LDH micro-nano fillers had a higher anticorrosion properties relative to the waterborne epoxy resins.

1. Introduction

Metal corrosion is becoming increasingly serious, resulting in serious environmental pollution and a serious waste of resources. The effective way to delay corrosion is the coating screen method [1]. Extensive studies have thus been conducted to improve the corrosion resistance of coatings [2–4]. One of the mitigation measures is the introduction of corrosion inhibitors and has achieved good results. However, this method will release a lot of volatile organic compounds (VOCs), polluting the environment. The other method is to use fluorocarbon resins with good corrosion resistance [5], but their price is too expensive to develop their further use in industry. Moreover, the surface of coatings are covered with a lot of micro-pores, which can't effectively block the corrosive medium [6], especially when waterborne resins are used as the substrate coating.

Water-borne epoxy resins are widely used as adhesives, coatings and composite matrix [7–8], because of their excellent adhesion, good chemical stability, and good corrosion resistance. However, water-borne epoxy resins will produce a large number of microporous during the high temperature curing process, resulting in the fast penetration of external corrosive media to the protected substrate, which seriously limits the application of water-borne epoxy resins in the industry [6]. Until now, the more effectively way to solve the problem is the use of micro-nano fillers in coatings, to effectively impede the generation of micro-pores caused by water evaporation during the coating process [9]. For this reason, the addition of nanofillers to water-borne epoxy resins to improve the corrosion resistance of coatings has been extensively studied. The former studies indicate that water-borne epoxy resins composites have good corrosion resistance, especially those containing lamellar micro-nano fillers [9–10].

When the inorganic material is incorporated with the polymer matrix, the composite material often fails due to the formation of the phase separation [11]. Therefore, in order to improve the compatibility of the inorganic material with the polymer system, the inorganic material usually needs to be modified [11]. Graphene is able to prevent oxygen and water molecules diffusion to the surface of meta-based materials due to its unique lamellar structure, and thereby protects the metal from oxidation-corrosion [12]. Graphene and its derivatives have been successfully used as preservative additives to improve the corrosion resistance of coatings [13–14]. However, the water dispersibility of graphene is still a challenge, especially its re-stacking, which seriously affects its applications [15–18]. Studies have shown that the addition of other nanomaterials to graphene composites significantly improve the performance of many aspects of graphene [19–20].

Layered double hydroxides (LDH) materials have a unique lamellar structure similar to the graphene, which have high metal dispersion, high surface area and thermal stability [21]. In recent years, nanocomposites based on graphene and LDH materials have been developed in the field of supercapacitors and catalysts [22]. Previous studies confirm

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Table 1
The main reagents and dosage in the preparation of rGO, ZnAl-LDH, rGO-ZnAl-LDH hybrid (x:1).

Samples	GO (mg)	$Zn(NO_3)_2\cdot6(H_2O)$ (g)	$Al(NO_3)_3\cdot9(H_2O)$ (g)	Urea (g)
rGO	50	–	–	5.76
ZnAl-LDH	–	2.082	1.125	5.76
rGO-ZnAl-LDH(1:1)	50	2.082	1.125	5.76
rGO-ZnAl-LDH(2:1)	100	2.082	1.125	8.64
rGO-ZnAl-LDH(4:1)	200	2.082	1.125	10.37
rGO-ZnAl-LDH(6:1)	300	2.082	1.125	11.52

that there is a good synergistic effect between rGO and the LDH layer [23]. Luo et al. prepared the reduced graphene oxide (rGO)/zinc aluminum layered double hydroxides (ZnAl-LDH) composite films on the surface of 6N01 aluminum (Al) alloy by a novel and facile hydrothermal continuous flow method, which showed an excellent corrosion protection compared with pure ZnAl-LDH [23].

Patil et al. used the graphene oxide and oxidized multiwalled carbon nanotubes as curing agents to induce cross-linking of an epoxy resin. The as-obtained composite exhibited an outstanding dispersion of the carbon nanomaterials compared with other methods [24]. These methods were complex and difficult to implement. Moreover, to the best of our knowledge, there is no report on anticorrosion coating of reduced graphene oxide zinc aluminum layered double hydroxides (rGO-ZnAl-LDH)/waterborne polymer composites.

In this study, graphene oxide (GO) was added into ZnAl-LDH with different ratios to form rGO-ZnAl-LDH, which were modified by 3-aminopropyl triethoxysilane and further put into waterborne epoxy resin and hardener as anticorrosive agent. The corrosion behaviors on the coated steel substrates were evaluated by electrochemical measurements and salt spray test. The effects of different GO: ZnAl-LDH ratios and the adding amount of rGO-ZnAl-LDH on the stability and anticorrosion of composite coatings were investigated.

2. Experimental procedure

2.1. Materials

Layered graphite was supplied by Gaotong Advanced Materials Co., Ltd., China. Waterborne epoxy resin (EP; NPEW-291W53; 51–55%; EE: 520–600 g/eq) and hardener (NPED-508; 66–70%; JIS: 210–240) were supplied by South Asia electronic material (Kunshan) Co., Ltd., China. 3-Aminopropyl triethoxysilane (APTES) was purchased from Nanjing union silicon Chemical Co., Ltd., China. All other chemicals, including concentrated sulfuric acid (98%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot6(H_2O)$), aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot9(H_2O)$) and urea ($CO(NH_2)_2$) were reagent grade and obtained from Sino pharm Chemical Reagent Co., Ltd., China.

2.2. Preparation of GO

GO was prepared by a modified Hummers' method [25–26]. In a typical process, 98% H_2SO_4 (50 mL) was added into a 250 mL flask at 0 °C (ice bath), followed by the addition of solid layered graphite (3.0 g) and $NaNO_3$ (1.5 g). And, $KMnO_4$ (9 g) was slowly put into the layered graphite suspension in 2 h. Then, the reaction temperature was adjusted to 35 °C and maintained for 30 min. After that, DI water (90 mL) was added dropwise to the mixtures at 90–95 °C, and H_2O_2 (30%, 40 mL) was added after 1 h. Finally, the solution was centrifuged, washed with HCl (5 wt%) and DI water several times and dried at 60 °C for 48 h. Mechanical stirring was used in the whole process. The as-obtained GO powder (50 mg) was ultrasonically dispersed in 100 mL deionized water for 3 h for further use.

2.3. Synthesis of rGO-ZnAl-LDH

The rGO-ZnAl-LDH hybrid was synthesized via a solution approach [19]. In this synthesis, 50 mg GO was used as 1 proportion, while 1 proportion ZnAl-LDH was based on 3 mmol $Al(NO_3)_3\cdot9(H_2O)$. The ratio of GO: ZnAl-LDH changed from 1:1 to 6:1. Firstly, the as-prepared GO suspension was dispersed ultrasonically again for 60 min. After that, 3 mmol of $Al(NO_3)_3\cdot9(H_2O)$, 7 mmol of $Zn(NO_3)_2\cdot6(H_2O)$ and appropriate quantity of urea (changing along with the amount of GO) were separately dissolved in 20 mL DI water, and then added dropwise to the GO suspension at 100 °C in 4 h. Subsequently, the suspension was further refluxed at 100 °C for 10 h with magnetic stirring. The pH of the system was adjusted to 8–8.5 by controlling the amount of urea. After the reaction, the black product was filtered by centrifugation, washed with deionized water several times until pH = 7.0, and dried at 60 °C for 12 h. The prepared samples were named as rGO-ZnAl-LDH (x:1), while x:1 was the ratio of GO: ZnAl-LDH. In this reaction, urea can not only adjust the pH value of the suspension, but also reduce GO to rGO. For comparison, the pure rGO and ZnAl-LDH were prepared at 100 °C for 14 h in the presence of urea (5.76 g) under the same experimental condition. The main reagents and dosage are shown in Table 1.

2.4. Preparation of M-rGO-ZnAl-LDH/EP composites

The surface of rGO-ZnAl-LDH was further modified by APTES because the unmodified powder can't be dispersed well in the resin.

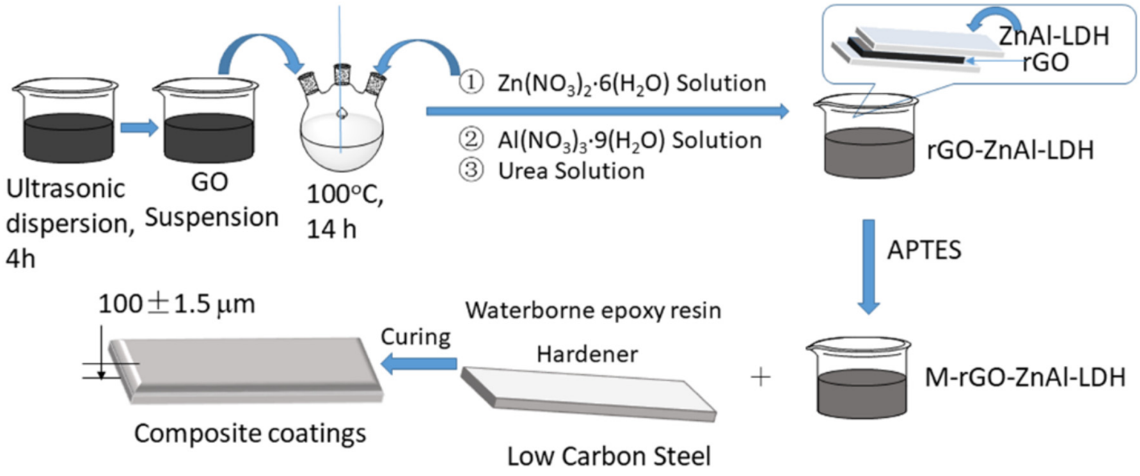

Fig. 1. Illustration of the preparation procedure of M-rGO-ZnAl-LDH/EP (x:1-y) composite coating.