



Achieving high performance corrosion and wear resistant epoxy coatings via incorporation of noncovalent functionalized graphene



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ABSTRACT

Graphene(G)-based polymer nanocomposites have attracted great interest owing to their superior physicochemical properties over polymers. However, the tendency of graphene sheets to aggregate makes it difficult to achieve homogenous dispersion in polymer matrix. Herein, by utilization of poly(2-butylaniline) (P2BA) as a dispersing agent, stable dispersion of graphene in organic solvents was achieved via non-covalent π - π interactions between P2BA and graphene nanosheets. The exfoliated graphene nanosheets were then integrated with coating matrix by curing reaction of epoxy resin with P2BA functionalized graphene (P2BA-G) and amine hardener. Embedding a small percentage of well-dispersed graphene nanosheets (P2BA_{0.5%}-G_{0.5%}) in epoxy coating remarkably improved anticorrosion performance and wear resistance properties, which was attributed to the synergistic effects of the redox catalytic capability of P2BA, high mechanical and barrier properties of well-dispersed graphene nanosheets in the epoxy matrix. The present study provides a promise strategy for development of graphene reinforced organic coatings with superior physical-mechanical properties for metal protection.

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1. Introduction

Owing to its unique structure and extraordinary electronic, thermal, mechanical and barrier properties, graphene has emerged as a promising two-dimensional material with numerous potential applications including batteries [1,2], capacitors [3], solar cells [4], nanocomposites [5], sensors [6,7] and coatings for corrosion prevention [8]. Extensive studies have demonstrated that graphene-based coatings are excellent anticorrosion barriers for metals [9–13]. For instance, Prasai et al. observed that graphene films directly grown on Cu and Ni by chemical vapor deposition (CVD) could serve as excellent corrosion resistant coatings [14]. Sahu et al. demonstrated that graphene coatings prepared by electrochemical deposition on a Cu substrate showed robust resistance to corrosion in a saline environment [15]. Koratkar and coworkers reported that

graphene coatings on Ni served as a passive layer that retarded microbially induced galvanic corrosion for extended periods over 2700 h [16]. Although the above references indicated that graphene coatings can protect metal against corrosion efficiently, the adverse effects of grain boundaries and defects of graphene prepared by CVD or electrodeposition on anticorrosion performance were also reported by Schriver et al. [17].

An alternative route for fabrication of graphene-based anticorrosion coatings is the incorporation of graphene nanosheets into polymer matrix to inhibit the diffusion of molecules through the coating by a tortuous way. In this case, the barrier properties of graphene are strongly affected by the dispersion and orientation of graphene platelets in the polymer matrix because the aggregated graphene through π - π interactions can induce coating defect and inferior barrier properties [18]. Therefore, a crucial step toward achieving high performance polymer/graphene composite coatings is to improve its dispersion and interface interactions in polymer matrix. Several research studies on chemical modification approaches have been reported to improve the dispersion of graphene in the composite coatings [10,19]. Li and coworkers reported on the fabrication of anticorrosive composite coatings on steel

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surface with waterborne polyurethane as the organic matrix and functionalized graphene oxide as the reinforcement [20]. The as-prepared coatings exhibited superior anticorrosion properties by adding 0.4 wt % of aligned graphene. Yeh and coworkers reported on covalent grafting of polyaniline (PANI) onto the surfaces of graphene by oxidation polymerization [10]. The formed composite coatings displayed outstanding barrier properties against O₂ and H₂O compared with neat PANI [10]. Recently, they also reported on the preparation of electroactive polyimide grafted graphene via a thermal imidization reaction [21]. The well-dispersed graphene/polyimide coatings provided advanced corrosion protection of cold-rolled steel as compared to neat polyimide coating. They explained the superior corrosion protection of graphene/polyimide coatings was due to redox catalytic capabilities of polyimide and barriers properties of high dispersed graphene in polyimide matrix.

Compared with the chemical modification of graphene, the noncovalent supramolecular approaches are particularly advantageous over chemical modification due to its less impact on the structure and properties of graphene, high efficiency and ease of preparation process [22]. Many efforts have been made to exfoliation of aggregated graphene into few layers in various organic solvents or aqueous solution via noncovalent functionalization approaches such as surfactants or aromatic compound mediated liquid phase exfoliation [23]. However, surfactants usually have limited graphene dispersion capacity [24] and the hydrophilic nature of surfactants may lead to inferior properties of the coating. The aromatic graphene dispersing agents are usually costly and difficulties in synthesis [25]. In present study, we demonstrated the utilization of poly(2-butylaniline) (P2BA) as noncovalent dispersant for preparation of graphene/epoxy anticorrosive coatings. P2BA possesses aromatic heterocyclic structures which can facilitate the dispersion of graphene in organic solvent through π - π interaction. Meanwhile, P2BA as a conducting polymer can protect the metal against corrosion through formation a passivated oxide layer at the interface of metal substrate and organic coatings [26]. Therefore, these synergistic effects of P2BA, graphene and epoxy resin are expected to enhance the corrosion protection performance of the as-prepared coatings. In this work, the dispersion of P2BA-functionalized graphene nanosheets in organic solvent was characterized by UV-vis, Raman spectroscopy, transmission electron microscope (TEM), and atomic force microscopy (AFM), respectively. The anticorrosion performance of graphene reinforced epoxy coatings on Q235 steel electrode was evaluated through a series of electrochemical corrosion measurements in 3.5 wt % NaCl aqueous solution. The tribological behaviors of the composite coatings were investigated on UMT-3 tribometer with a ball-on-plate configuration under dry conditions.

2. Experimental section

2.1. Materials

2-butylaniline and ammonium persulfate were purchased from Aladdin Industrial Corporation. Tetrahydrofuran (THF), ethanol, ammonium hydroxide (NH₄OH) and hydrochloric acid (36%–38%) were purchased from Sinopharm Chemical Reagent Co. Ltd. All commercial chemicals and solvent were used as received without further purification. Graphene was purchased from Institute of Coal Chemistry Chinese Academy of Sciences. Epoxy resin (E44) and curing agent (H-4 polyamide) were purchased from Yunda Chemical Co., Ltd. China.

2.2. Synthesis of poly (2-butylaniline) (P2BA)

The P2BA was synthesized in a similar procedure reported by

Liao et al. [27]. 2-butylaniline (7.46 g, 50 mmol) was dissolved in 1.0 M HCl solution (250 mL) at 0 °C, then ammonium persulfate (11.41 g, 50 mmol) in 1.0 M HCl solution (100 mL) was added in one pot. The reaction mixture was stirred for another 1 min to ensure complete mixing. Subsequently, the reaction was allowed to proceed without agitation for 24 h at –5~0 °C. Finally, the crude product was dedoped with 0.1 M NH₄OH, washed with distilled water and ethanol until the filtrate became colorless, and then dried in a vacuum at 40 °C to a constant weight.

2.3. Preparation of P2BA-G dispersion

Typical procedure for preparation of the P2BA stabilized G suspensions is as follows. A given amount of P2BA was dissolved in THF with sonication for 0.5 h to obtain a homogeneous dark blue solution, then precalculated graphene was added to P2BA THF solution and was ultrasonicated for 3 h to get P2BA stabilized G suspension. In this study, the optimum weight ratio of P2BA to G is 1:2.

2.4. Preparation of composite coatings

Before coating, the Q235 steel (chemical composition was shown in Table S1) electrode surface was polished with 400, 800 and 1500-grit of sandpapers, and was then rinsed by distilled water. After being degreased by ultrasonication in acetone, it was finally dried with nitrogen and kept in a desiccator prior to painting. The G-based epoxy composite coatings were prepared in the following procedures. A precalculated epoxy 44 was added to the P2BA-G suspension containing given amount of G. After being carefully stirred for 10 min, THF was removed by rotary evaporation. The curing agents (25 wt % of epoxy 44) were added and the mixtures were mixed thoroughly with high speed blender (PI7500 R75G1, POWTRAN) at 4000 rpm for 5 min. After that it was degassed in a vacuum oven at room temperature to remove the trapped air bubbles and ready for different coating samples. According to the weight content of P2BA and G, the composite coatings were named as P2BA_{0.5%}-G_{0.5%}, P2BA_{0.5%}-G_{1%}. For comparison purpose, P2BA_{0.5%} and pure epoxy coating were prepared via the similar procedure. Two different kinds of coating samples were prepared for the corresponding measurements: (1) all various components were coated on Q235 steel electrode with a wire bar coater, and the samples were cured at room temperature for 3 days. These samples were used for electrochemical measurements. The coating thickness was 20 ± 2 μ m measured by using a PosiTector6000FNS1 apparatus. (2) The free-standing films were obtained through curing reaction in a PTFE mold for 24 h under 40 °C and were cut into the dimension of 20 mm \times 60 mm \times 2.0 mm for gravimetric experiment.

2.5. Characterization

UV-vis spectrum (Lambda 950) and Raman spectra (Renishaw inVia Reflex) were used to characterize P2BA-G hybrid. The chemical composition was determined by X-ray photoelectron spectroscopy (XPS) measurement (AXIS ULTRA DLD) with a monochromated Al K α irradiation. The microstructure and morphology of P2BA, and P2BA-G hybrid were examined by scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscope (TEM, JEM-2010). The thickness of graphene was identified by a tapping mode atomic force microscopy (AFM, Dimension3100 V). The morphology of the P2BA-G hybrid in epoxy matrix was also verified by using both SEM and TEM. The corrosion products formed on the Q235 substrates were characterized by SEM (EDS) and XRD (D8 Advance, Bruker). The scans of XRD measurement were performed in a 2 θ range of 10–90° with a scan

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