



Processable poly(2-butylaniline)/hexagonal boron nitride nanohybrids for synergetic anticorrosive reinforcement of epoxy coating

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ABSTRACT

Hexagonal boron nitride (h-BN), a structural analogue of graphene, is a better alternative for anticorrosive coatings because of its electrical insulation properties. In this work, few-layer h-BN nanosheets are obtained by the exfoliation of stacked h-BN powders with poly(2-butyl aniline) (PBA) and incorporated into epoxy coatings for protecting metallic substrate against corrosion. Results show that as prepared composite coatings exhibit high impedance modulus and low water absorption, suggesting their superior performance of corrosion protection owing to the “labyrinth effect” of h-BN and passivation effect of PBA on the metal substrates.

1. Introduction

Organic coatings are widely applied for corrosion protection of metal substrates, which can serve as the barrier to delay the corrosion of metal substrates [1–4]. However, solvent evaporation during film formation process could lead to the creation of micropores and pinhole defects within the coatings, which makes the coating more permeable to corrosive medium. Additionally, long-term exposure to the corrosive environment results in pore formation due to the leaching of the coating components, therefore, accelerating the coating damage and metal corrosion [5,6]. Various approaches have been attempted to improve the barrier properties of organic coatings. Among them, incorporating nanofillers into the organic coatings has been identified as an effective way to improve their long-term corrosion protection [7]. It has been reported that organic coatings containing nanofillers (clay, SiO₂, TiO₂, ZnO, Al₂O₃ and Fe₂O₃) exhibit enhanced corrosion protection to metal substrates by improving their barrier properties [7–11].

With the development of carbonaceous nanomaterials, the discovery of single-atomic-layer graphene has triggered extensive research interest owing to its outstanding thermal, mechanical, electrical and extremely impermeable properties. Graphene has been explored in many applications including polymer composites [12], energy storage [13], coatings [14], and biomedical engineering [15,16]. In the field of corrosion, up to now, a number of papers and patents have been dealt with the use of graphene as corrosion or oxidation resistant coatings

[17,18]. However, the high electrical conductivity of graphene may lead to galvanic corrosion between the graphene and the underlying metal substrates over long-term immersion in corrosive medium, which could accelerate the degradation of metal [19,20]. Hexagonal boron nitride (h-BN), also called “white graphene”, possesses features analogous to graphene, such as high impermeability, mechanical properties and thermal conductivity [21]. However, one important difference between h-BN and graphene is that h-BN is an electrical insulator with a large band gap due to the high electronegativity of nitrogen [22,23]. Hence, there is little probability of galvanic corrosion between h-BN and the underlying metal substrate [24–26]. Shen et al. evaluated the long-term barrier properties of CVD-deposited h-BN and graphene monolayers, and confirmed that the monolayer h-BN was a better alternative to graphene for long-term corrosion protection of metal substrates [25]. Although h-BN films grown by CVD possess many superior properties, their applications are still hampered due to the difficulty in growing large area h-BN films without defects and grain boundaries at arbitrary substrates [27]. A feasible approach to achieve the wide application of h-BN is to incorporate the layered h-BN into polymer matrix to integrate its barrier properties with the ease of fabrication of polymer matrix. In this aspect, exfoliating the stacked h-BN into few layered nanosheets is the key for achieving better dispersity within coating matrix. However, the interlayers of h-BN are closely packed by the attractive forces from the pseudo-delocalized out-of-plane π orbital and Van der Waals interactions, which make it more difficult to exfoliate h-

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BN into few layers with low defects. In most cases, harsh chemical processes are necessary to achieve scalable products of h-BN nanosheets [28,29]. Recently, several reports have been presented on the exfoliation of h-BN by non-covalent interactions between h-BN and surfactant, aromatic polymers or biomolecules, which could avoid the destruction of the intrinsic bonding structure and maintain the physical properties of h-BN [30,31].

Up to now, extensive investigations have been performed on the general electrochemical properties of graphene coatings [32–34] and graphene/polymer composite coatings [35,36], as well as the comparison between h-BN and graphene [25], however, what is lacking in the literature is the investigations on the effects of exfoliated h-BN nanosheets for long-term corrosion protection of the metal. In this work, we aim to develop the epoxy nanocomposite coatings with enhanced corrosion protection through incorporating non-covalently exfoliated h-BN nanosheets. To achieve this goal, poly(2-butyl aniline) (PBA) is synthesized as a non-covalent dispersant for liquid-phase exfoliation of h-BN. The novelty of this work is that PBA can not only exfoliate the stacked h-BN into a few atomic layers but can also act as the corrosion inhibitor to delay the corrosion by passivating the metal substrates. All in all, significant enhancement in corrosion protection of the coatings will be obtained in this way. The corrosion protection and barrier properties of the epoxy nanocomposite coatings are evaluated under 3.5 wt% NaCl solution by electrochemical methods and the water absorption test. The corroded metal surface is also analysed to further investigate the corrosion mechanism of the composite coatings.

2. Experimental section

2.1. Materials

Aniline dimers, 2-butyl aniline, ammonium persulfate, tetrahydrofuran (THF), ammonium hydroxide and concentrated hydrochloric acid (HCl) were purchased from Aladdin Industrial Corporation. Hexagonal boron nitride nanosheets (h-BN, 99%) were purchased from Sigma-Aldrich. Epoxy resin (E44) and curing agent (650 polyamide hardener) were purchased from Xuee Resin Factory, Wujiang City and Yunda Chemical Co. Ltd. China, respectively. Q235 carbon steel electrodes (volume: 1 cm³) were selected for the corrosion study. The detailed preparation began by the ultrasonic cleaning of Q235 carbon steel substrates with acetone and ethanol for 1 h to remove grease and contaminants on the surface, and then, the substrates were dried with a nitrogen flow. The Q235 carbon steel substrates were then welded to copper wire and placed on the bottom of circular-plastic vessels. Subsequently, epoxy resin paints were injected into the above vessels and cured at room temperature for 24 h. As a result, only one surface of the substrate was exposed to air (exposed area: 1 cm²) and other surfaces were sealed by epoxy resin. Finally, the surface of the electrode was mechanically polished with 800 and 1500 grit of SiC abrasive paper, respectively, then ultrasonically cleaned in acetone and ethanol, and dried in air.

2.2. Synthesis of poly (2-butyl aniline) (PBA)

Aniline dimer (153 mg) was added into a mixed solution of ethanol and HCl (1.0 M, 100 mL). After that, 2-butyl aniline (5 g) was added to the above mixture with continuous stirring. A solution of ammonium persulfate (11.41 g) in HCl (1.0 M, 100 mL) was added very quickly to the mixed solution with rapid stirring (10 s), and the final mixture was equilibrated at room temperature for 24 h. The mixture was filtered and washed with water to collect the crude PBA, which was washed with hydrazine (10 wt%) and deionized water several times. Finally, the products were dried at 60 °C under vacuum until a constant weight was measured.

2.3. Preparation of coating

Specific amounts of PBA and h-BN powder were first added in THF (10 mL) with continuous ultrasonication for 30 min at room temperature. Subsequently, 10 g of epoxy resin was added to the mixture with ultrasonication to obtain a uniform mixture. Then, the solvent in the mixture was removed by rotary evaporation. Afterwards, 2.5 g of polyamide hardener was added, and the mixture was vigorously stirred for 10 min, whereby degassing was performed with a vacuum pump at room temperature for 10 min to remove the air bubbles. The final mixture was applied on the surface of Q235 steel electrodes by a wire bar coater with a thickness of approximately 20 µm. The samples were first kept at room temperature for 2 h and then cured in an oven at 80 °C for 2 h. The epoxy nanocomposite coatings with different contents of h-BN nanosheets (0, 0.5 wt%, 1.0 wt% and 2.0 wt%) were prepared in a similar manner and named as the neat epoxy, BN_{0.5}EC, BN_{1.0}EC and BN_{2.0}EC, respectively.

2.4. Basic characterization

The structure of PBA was identified by Fourier transform infrared spectroscopy (FTIR, NICOLET 6700, Thermo, America). The interaction between h-BN and PBA was demonstrated by UV–vis absorption spectroscopy (Lambda 950, Perkin-Elmer, America) and Raman spectroscopy (Renishaw inVia Reflex, Renishaw, United Kingdom). The morphology of the exfoliated h-BN nanosheets was observed by transmission electron microscopy (TEM, JEM2100, JEOL, Japan) and scanning probe microscopy (SPM, Dimension 3100, Veeco, America). To evaluate the dispersion of h-BN in epoxy coatings, the surface and fracture surface of the neat epoxy and BN_xEC systems were examined by field emission scanning electron microscopy (FESEM, S-4800, HITACHI), where the coatings were coated by Au sputtering. The dispersion quality of h-BN in epoxy matrix was also examined by TEM (JEM2100, JEOL, Japan).

2.5. Electrochemical measurements

The electrochemical properties of the coatings were evaluated by open circuit potential (OCP) test and electrochemical impedance spectroscopy (EIS) in a conventional three electrode cell using an electrochemical work station (CHI660E, Chenhua, Shanghai). A saturated calomel reference electrode (SCE), a platinum sheet and coated electrode with an exposed surface area of 1 cm² were used as the reference electrode, counter electrode and working electrode, respectively and 3.5 wt.% NaCl solution was used as the corrosive medium. The OCP of system at the equilibrium state was recorded for 30 min. The EIS measurements were performed at different immersion times over a frequency range of 100 kHz to 10 mHz with an AC amplitude of 10 mV at OCP. Zview software was used to fit the EIS results. In the electrochemical investigations, three parallel samples were used for each coating to ensure the reproducibility.

2.6. Analysis on the morphology and structure of substrate after corrosion

After the long-term immersion in 3.5 wt.% NaCl solution, the coating was removed from the electrode, and the surface of Q235 steel substrate was analysed by SEM (EVO18, ZEISS, Germany) and X-ray diffraction (XRD, D8 Advance, Bruker AXS, Germany) equipped with Cu Kα radiation.

2.7. Water absorption

Water absorption of the epoxy nanocomposite coatings was evaluated by the gravimetric methods according to Eq. (1) [37,38]. The masses of the free films were measured at different immersion times using a Mettler Toledo AL204 microbalance (10^{−4} g resolution). When

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