Composites Science and Technology 129 (2016) 30–37

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Reinforcement of graphene and its derivatives on the anticorrosive properties of waterborne polyurethane coatings

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ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form
8 March 2016
Accepted 14 April 2016
Available online 21 April 2016

Keywords:
Nano composites
Coating
Polymer-matrix composites (PMCs)
Corrosion
Graphene

ABSTRACT

Graphene oxide, mildly reduced graphene oxide (RGO) and functionalized graphene were added to waterborne polyurethane (PU) matrix as the anticorrosive reinforcement, respectively. The anticorrosive properties of the graphene oxide and its derivatives reinforced PU composite coatings were characterized by Electrochemical Impedance Spectroscopy (EIS) and salt spray tests. The dispersion states of graphene in PU matrix varied with the chemical states of graphene. The correlations between the chemical states, dispersion states of graphene, and anticorrosive properties of the composite coatings were discussed. The superior anticorrosive properties of the graphene reinforced PU composite coatings were achieved by the addition of 0.2 wt% of RGO. The EIS results showed that the under-painting corrosion did not occur after 235 h immersion in 3.5 wt% NaCl electrolyte and the impedance modulus at 0.1 Hz remained at 10^9 Ω, barely changed for 235 h.

1. Introduction

As an anticorrosive additive, graphene has its unique characteristics, including geometric properties (two-dimensional shape, high aspect ratio, flexibility); high mechanical properties, high transparency as well as chemical and thermal stability. Research efforts have been made on the applications of graphene as anticorrosive barriers.

The barrier properties of graphene film grown by chemical vapour deposition were proven on copper surfaces by its anticorrosive properties [1], although the long-term anticorrosive properties of the graphene film were decayed, due to the large number of defects of the graphene film [2]. It was difficult to fabricate large-area defect-free graphene films suitable for industrial applications. Therefore, a multilayer graphitic films based on reduced graphene oxide were proposed, which was found highly impermeable to all gases, liquids and aggressive chemicals [3]. Alternatively, graphene and its derivatives reinforced polymer matrix composites have attracted particular interest for their barrier properties [4–7]. Byung Min Yoo et al. reviewed the barrier applications of graphene, graphene oxide (GO) and graphene reinforced polymer composites [8]. It was reported that the oxygen permeability [4,5,9], carbon dioxide permeability [5], nitrogen permeability [6], moisture permeability [7], helium permeability [10] and hydrogen permeability [11] of polymer-matrix composite film could be significantly reduced with the addition of a certain amount of graphene and its derivatives. One of the applications of polymer composites with enhanced barrier properties was the protective organic coatings. It has been shown that the anticorrosion properties of polymer composite coatings could be improved by the addition of graphene as reinforcements [12–14].

Waterborne organic coatings are gradually replacing coating formulas with organic solvent to reduce the discharge of volatile organic compounds. Waterborne polyurethane (PU) has been widely used as the organic binder in anticorrosion coatings due to its high flexibility, excellent abrasion resistance and chemical resistance, as well as the strong adhesion to substrates. The effect of the nanofillers, like carbon nanotubes [15], nanoclay [16], graphene [17], has been studied on the anticorrosive properties of PU matrix coatings. The improved anticorrosive properties of the composite coatings were attributed to the barrier properties of the nanofillers. It was emphasized by the experimental studies that the dispersion, orientation and aspect ratio of nanofillers were critical factors on the anticorrosive properties/barrier properties of the composite coatings.

Theoretical studies have been presented on the nanofillers

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http://dx.doi.org/10.1016/j.compscitech.2016.04.017

(nano-rods, nanotubes, nano-disks and nanoplatelets) reinforced polymer composites. The tortuosity model and percolation theory were proposed to predict and evaluate the possibility of barrier network formation [18]. The increased barrier properties of composites were explained by the elongated pathway of the foreign molecules. The critical amount of the filler to form the barrier network was defined as the percolation threshold. A series of theoretical studies was based on the renormalization group theory to quantitatively evaluate the effects of geometric factors, such as aspect ratio and orientation of clay platelets, on the barrier properties of clay/polymer nano composites [18]. Besides, another theoretical study explored the dependence of percolation threshold of random oriented rods/disks on their aspect ratios, based on excluded volume approach [19]. We also presented previously the theoretical study based on interparticle distance model, focusing on the effects of dispersion state and aspect ratio of graphite nanoplatelet/carbon nanotubes on the percolation threshold of their polymer composites [20,21].

In the view of the above literature, our current study was focused on the fabrication of high aspect ratio well dispersed graphene reinforced waterborne PU composite coatings, aiming for their exceptional anticorrosive properties. The present paper was a continuation of our previous studies [17,22,23] on fabrication of high aspect ratio GO, reduction and functionalization of GO and their application in composite coatings.

2. Experiments

2.1. Graphene oxide and functionalized graphene

GO was prepared by modified Hummers method, as reported previously [22,23]. The as-prepared GO had a thickness of about 1 nm and a lateral size ranging from several microns to several hundred microns, which tended to have much higher aspect ratio than other nanofillers, like nanoclay or graphite nanoplatelets.

Functionalized graphene (FG) was fabricated by simultaneous reduction and functionalization of GO with microwave-assistance [22]. Typically, 100 ml GO/DI water solution (1 mg/ml) was mixed with 5 ml hydrazine hydrate (85%) and 0.5 g titanate coupling agent (TM-200S, Yangzhou Tianyang Auxiliaries Co. Ltd.). The mixture was treated while stirring using a microwave reactor (CEM, Discover SP) at 120 °C for 10 min, followed by filtration and flush with DI water repeatedly to eliminate the unreacted titanate coupling agent and hydrazine hydrate.

2.2. Preparation of the GO, mildly reduced GO and FG reinforced PU composite coatings

The aqueous dispersion of GO or FG was mixed with waterborne PU (NeoRez R-9679, DSM, the solid content is 37 wt%). A certain amount of DI water was added to obtain a solid content of the liquid paintings as 20 wt%. The mixture was stirred magnetically for 30 min, then the GO or FG reinforced liquid paintings were obtained. For mildly reduced GO (RGO) reinforced paintings, a small amount of hydrazine (GO: hydrazine weight ratio was 1: 2.5) was added to the mixture of GO/PU liquid paintings. Electrogalvanized steel (EG) sheets (80 mm × 40 mm × 1 mm), supplied by Baosteel Ltd. (Shanghai), were thoroughly cleaned by sonication in alkaline degreaser (Henckle, Shanghai) for 10 min, flushing using DI water and sonication in ethanol for another 10 min. The liquid paintings were applied on the EG surfaces with a bar coater, and then the specimens were baked in a vacuum oven at 110 °C for 30 min to obtain the corresponding composite coatings.

2.3. Characterizations

A transmission electron microscope (TEM, FEI Tecnai G2 SpiritBiotwin) was used to evaluate the nanoscopic dispersion states of graphene in PU matrix at an acceleration voltage of 120 kV. For TEM sample preparation, a free-standing graphene reinforced PU composite thin film was embedded in an epoxy matrix and microtomed (Leica UC6) into 100 nm thick slices with a diamond knife. The cryogenic fracture surfaces of the coated EG sheets were observed using a scanning electron microscope (SEM, Quanta FEG450).

For the Electrochemical Impedance Spectroscopy (EIS), a three-electrode cell was used: the coated EG surface as the working electrode with an exposed area of 1 cm^2, the saturated Ag/AgCl (0.205 V vs. SHE) as the reference electrode and a platinum counter electrode. The electrolyte was a 3.5 wt% NaCl solution (reagent

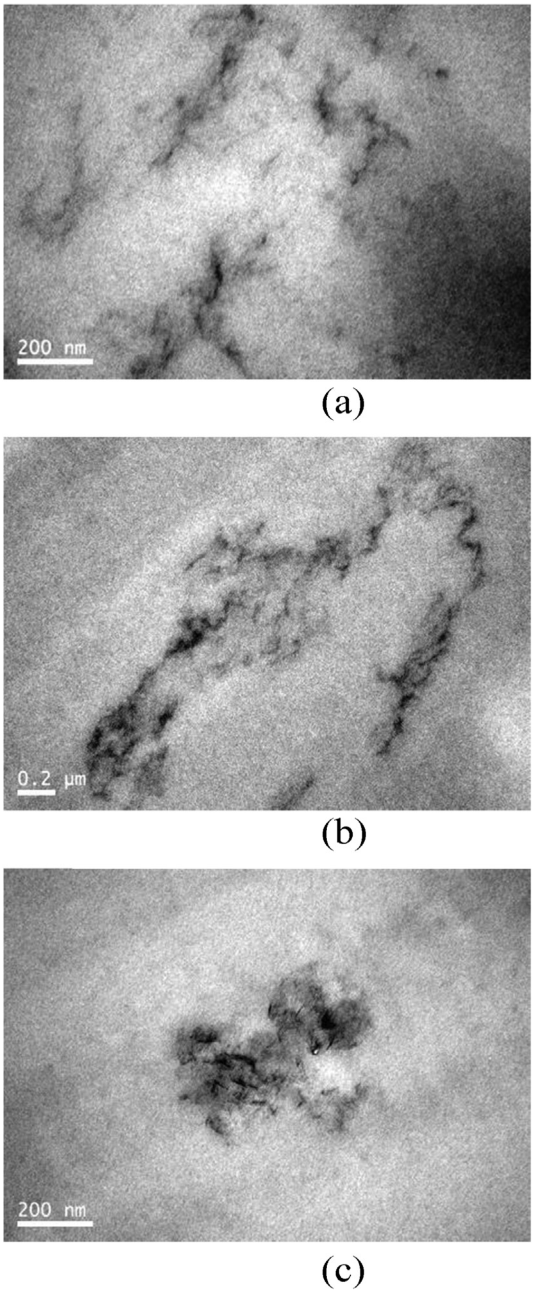

Fig. 1. TEM images of GO (a), RGO (b) and FG (c) reinforced PU composite coatings.