Composites Communications 9 (2018) 6–10

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Functionalized graphene/polymer composite coatings for autonomous early-warning of steel corrosion

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ARTICLE INFO

Keywords:
Early-warning
Self-sensing
Graphene
Composite coatings

ABSTRACT

Corrosion protection coatings with autonomous early-warning functions can prevent catastrophic failure of steel structures. We prepared a self-sensing polymer composite coating with functionalized graphene oxide. The graphene oxide (GO) was chemically modified with 1, 10-phenanthroline-5-amine (phen), which can form a red complex with Fe^{2+}, so as to give a signal of corrosion reaction at very early stage. The waterborne polyurethane (PU) was employed as the environmental-friendly coating matrix. The dispersion of the phen-modified GO in the PU matrix was promoted by the addition of laponite RD. The composite coatings with functionalization GO and laponite RD showed higher corrosion resistance than the pure PU coatings, as characterized by salt spray test. Before the accumulation of Fe^{3+} on the steel plates, the red color change was observed for the composite coatings, showing the onset of the corrosion reaction.

1. Introduction

Steel corrosion causes loss in material properties and may pose threat to structural safety, like railways and bridges. It is highly desired to develop a method to mitigate the corrosion reaction, while provide autonomous early-warning by detecting the corrosion reaction at early stage, so that the requirement of maintenance can be clearly seen in advance.

Research efforts have been directed to the detection of corrosion reaction beneath the polymer coatings, such as instrumental inspections using ultrasonic, thermal imaging, and electrochemical spectrum. Some self-sensing technology was realized through the coating formulation [1]. Usually, a pH indicator or a radical indicator was included in the coating formulation, which interacted with the corrosion products at metal-coating interface and showed color or fluorescence change [2]. Dhole et al. used different derivatives of 1, 10-phenanthroline-5-amine (phen) to chemically modify different polymer chains [3,4]. The synthesized polymers will react with Fe^{2+} and turn into red color. Microcapsule-based corrosion sensing technics were also reported. For example, a pH-indicator, phenolphthalein, was encapsulated to detect the pH change during the corrosion reactions [5]. The microcapsule-based technics can be applied to detect micro-cracks in polymeric coatings [6]. Here, we proposed a facile molecular grafting method. The corrosion indicator molecules were grafted onto graphene oxide (GO) surfaces, so that the corrosion indicator can distributed in varies polymeric matrix with the functionalized GO while preparing the composite coatings.

Graphene, a two-dimensional graphitic carbon material, has high aspect ratio and excellent barrier properties. Graphene and its derivatives have been applied as the barrier reinforcement in polymer matrix coatings, aiming for enhanced anticorrosion properties and other properties [7–9]. The re-stacking and agglomeration of graphene sheets were the major challenge for the graphene reinforced composite coatings [10]. The dispersion of graphene sheets was usually promoted through covalent or non-covalent bonding, such as polymer-grafting, coupling treatment [11,12] and surfactant wrapping [13]. Moreover, a series of nano-particles were employed to assist the dispersion of graphene sheets, like LDH [14], montmorillonite clay [15] and laponite clay [16].

GO has high chemical reactivity due to the presence of the large amount of oxygen functional groups. In this paper, phen was employed as the corrosion indicator, which was grafted on GO surfaces, so that the phen can distribute in polymer matrix with graphene layers.

2. Experimental

2.1. Materials

GO was prepared by modified Hummers method, as described previously [17]. Laponite RD (laponite) was kindly supplied by BYK

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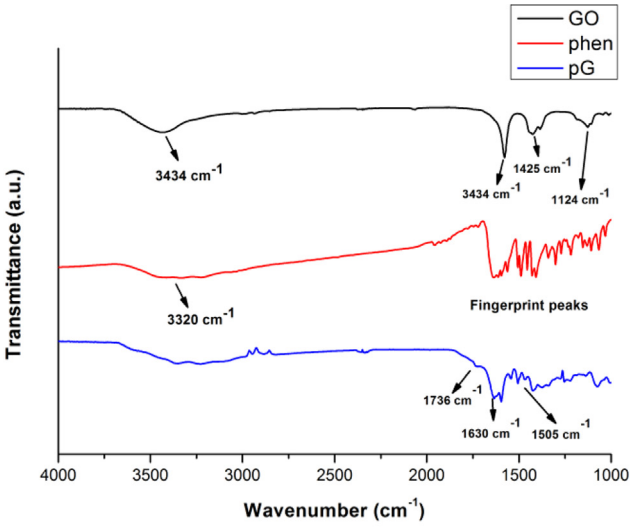
https://doi.org/10.1016/j.coco.2018.04.002
Received 28 February 2018; Received in revised form 5 April 2018; Accepted 8 April 2018



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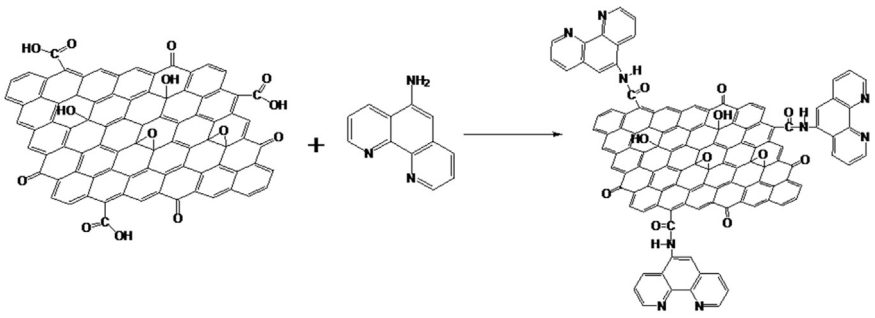

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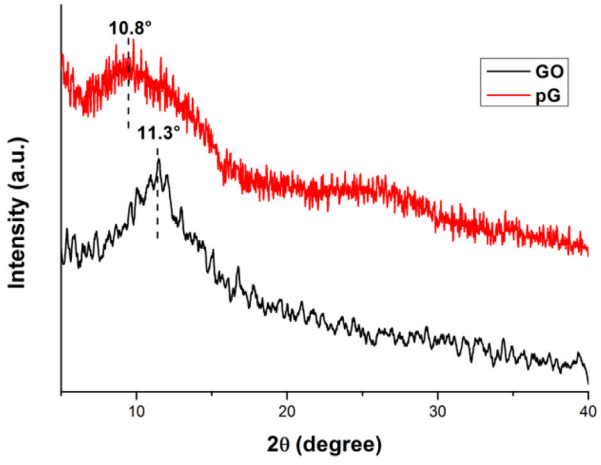

(c)

Fig. 1. (a) FTIR spectra of GO, phen and pG; (b) reaction schematics between phen and GO; (c) XRD spectra of GO and pG.

Additives & Instruments. The silicate platelets of laponite have a diameter of 25~30 nm and a thickness of 1 nm. As received laponite powder was mixed with DI water at a concentration of 20 mg/ml by high shear mixing at 600 rpm for 30 min to obtain a transparent suspension. Anionic waterborne polyurethane (PU) with a solid content of 27 wt% was supplied by Huayi Fine Chemical Ltd., Shanghai.

2.2. Modification of GO by phen

5 ml water dispersion of GO (2 mg/ml) was mixed with 10 mg phen. The mixture was sonicated for 30 min in a bath sonicator and then treated while stirring using a microwave reactor (CEM, Discover SP) at 80 ℃ ~140 ℃ for 20 min. The mixture were centrifuged at 11,000 rpm