Carbon 101 (2016) 315–323

Contents lists available at ScienceDirect

Carbon

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

Functionlized graphene serving as free radical scavenger and corrosion protection in gamma-irradiated epoxy composites

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ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form
11 January 2016
Accepted 1 February 2016
Available online 2 February 2016

ABSTRACT

Epoxy networks, as common protection materials, possess some adverse degradation effects in the gamma irradiation environment, which greatly limit their potential applications for metal protection in nuclear industry. To avoid this, we attempted to incorporate the graphene oxide (GO) with significant radical scavenger behavior into the epoxy resin, followed by thermal polymerization to obtain the functional graphene oxide/epoxy nanocomposite coating (GEP). The electron spin resonance (ESR) detection shows that graphene can act as radical scavenger, and a relatively small quantity (0.25 wt%) addition of graphene within the epoxy resin exhibits the least amount of radicals. In addition, electrochemical data strongly demonstrate that graphene is capable of maintaining the anti-corrosion properties under the gamma irradiation environment. Therefore, the designed hybrid GO/epoxy resin composite can be considered as promising candidates for protective coatings in nuclear industry.

1. Introduction

Epoxy networks like diglycidyl ether of bisphenol-A epoxy resins are widely used as long-term protective coatings in various industrial fields, especially nuclear industry [1]. However, some environmental factors, such as γ-radiation, temperature, and atmosphere [2,3], could cause the structural deterioration of the epoxy coating and greatly damage its properties, which leading to the reduced service life. In many cases, as an electromagnetic radiation of high frequency [4], γ-radiation is one of the most principal degradation processes. Under γ-radiation, the surface of the epoxy coating would generate the cracks and blistering due to the radiolytic degradation [5], finally resulting to the reduced anti-corrosion properties of the epoxy networks [6–8]. In addition, nuclear industrial materials always suffer more or less permeation of the corrosive agents (oxygen, water and ions) after exposure to a wet or humid environment. These corrosive agents can gradually permeate onto the metal interface, which could decrease the coating adhesion and final accelerate corrosion of the metal substrate [9]. Therefore, it is necessary to find a composite material which is not only resistant to a certain amount of γ-ray irradiation but has the excellent anticorrosive performance in this unusual environment.

Graphene and derivatives have garnered the most interest for nanomaterials due to their distinct advantages with respect to unique mechanical, electrical, thermal conductivity, thermal stability, chemical inertness, electromagnetic interference, gas barrier properties and impermeability to small ions and molecules [10]. They have been extensively reported to be used in various applications, such as nano-biocatalysis [11], advanced gas barrier polymer composite films [12] and ideal photocatalyst carrier [13]. Recently, a variety of promising materials serving as anti-γ-ray coating and the mechanisms of the irradiation on the materials have been proposed [14–19]. For example, Djouani et al. [4] reported epoxy networks based on diglycidyl ether of bisphenol-A (DGEBA) cured with POPA was irradiated at 25 °C in air and found that the C–C and C–H bonds of DGEBA can be broken apart due to the formation of the radicals, which can promote the degradation of the epoxy resin and result in reduced protective performance. Zan et al. [20] used graphene-encapsulated MoS_2 to fabricate the “sandwiched” sample like graphene/MoS_2/graphene and also proved that graphene could improve the stability of the “sandwich” under the condition of radiation. Martinez-Morlanes et al. [16] found that MWCNTs were capable of maintaining the efficiency of the crosslinking density of ultrahigh molecular weight polyethylene (UHMWPE). Electron spin resonance detection of the radiation-induced radicals proved the radical scavenger behavior of

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http://dx.doi.org/10.1016/j.carbon.2016.02.004
0008-6223/

MWCNTs: when the nanotube concentration increased, the number of radicals generated by the gamma irradiation process decreased. Therefore, both graphene and MWCNTs can improve the stability of the nanocomposites under the irradiation environment. What is more, graphene could significantly improve the anti-corrosion properties [21–26]. Compared to other reinforcement materials, graphene exhibited the enhanced physicochemical behaviors with light-weight components at the much lower load than other metal oxides and ceramic reinforcement [27–30]. The outstanding performance is attributed to the addition of functional graphene oxide, which can increase the tortuosity of the diffusion pathways to effectively prevent H_2O and O_2 from accessing the substrate surface, thus leading to a super anticorrosion property [26,31,32]. However, during the γ-ray irradiation process, the change of anti-corrosion properties of graphene-epoxy composites is seldom studied and still unclear.

In this paper, graphene oxide (GO) was firstly functionalized via surface modification, which is beneficial to obtain the homogeneous dispersion and strong filler–matrix interface in epoxy resin [27]. Then, we tried to incorporate the graphene oxide (GO) into the epoxy resin, followed by thermal polymerization to obtain the functional graphene oxide/epoxy nanocomposite coating (GEP). In order to explore the stability of GEP under γ-ray irradiation, both the neat epoxy resin and the graphene-based composites were gamma-irradiated by different dosage. Then the electron spin resonance spectroscopy (ESR) was used to study the radical formation in irradiated neat epoxy and GEP samples. At the same time, the anti-corrosion properties after the γ-ray irradiation were mainly studied by the potentiodynamic polarization and electrochemical impedance spectrum (EIS).

2. Experimental section

2.1. Synthesis of the EPTES functionlized graphene oxide (FGO)

The preparation process for the fabrication of GEP coating materials is shown in Fig. 1(a). As mentioned above, graphene oxide was purchased from Nanjing XFNano Material Tech Co. The γ-(2,3-epoxypropoxy) propytrimethoxysilane (EPTES) functionlized Graphene Oxide (FGO) was achieved in a mixture of water/ethanol (25/75 by volume). A quantity of 10 mg of KH560 was first introduced into 100 ml of the mixture of water/ethanol, acetic acid was adopted to adjust pH, the pH value is buffered closed to 3.5. Then 0.10 g GO were added into the mixture of water/ethanol, and the grafting reaction was realized under oil-bathing for 24 h at 80 °C.The reaction product was filtered and washed by using a mixture water/ethanol and dried at room temperature.

2.2. Preparation of functional graphene oxide/epoxy nanocomposite thin film and its coating on carbon steel for corrosion prevention

The functional graphene oxide/epoxy nanocomposite which named as GEP was prepared by dispersing FGO in 7.0 g n-butylalcohol then ultrasonicated for 3 h and added into 10.0 g DGEBA together with a predetermined curing agent POPA (DGEBA and curing agent were in a 10:3 equivalent). The FGO powder was well dispersed in DGEBA, and no settlement was observed, even after a month. To verify the optimum content of FGO for the best corrosion performance of the nanocomposites under the γ-irradiation, we made the composites by varying the content of FGO in 10.0 g DGEBA, using: 25, 50 and 75 mg. In the next step, the treated carbon steel panels were dipped into the ink-like liquid mixture. Subsequently, the coated samples were pre-cured at 120 °C for 3 h, and post-cured at 180 °C for 3 h. The thickness of the coating was about 15 μm, and the thickness of the resulting film was measured by thick tester (FILMETRICS, F20). After curing, the surface color of the FGO/DGEBA composites coated samples became golden brown, which was used as a visual test for evaluating the anticorrosion efficiency of the coating. Similar, the same coating procedure was followed for the preparation of only DGEBA-POPA (neat epoxy) coated carbon steel panels.

2.3. Irradiation experiment

Irradiation by ^{60}Co gamma rays was performed at 25 °C in air with rates of 0.78 kGy h^{-1} and the range of irradiation is from 40 to 280 KGy.

2.4. Physical characterization

The field emission scanning electron microscopy (FE-SEM) images were obtained using Hitachi S-4800 microscope with an acceleration voltage of 30 kV. Transmission electron microscopy (TEM) images were captured on a JEM-2100 instrument microscope at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker D8 X-ray

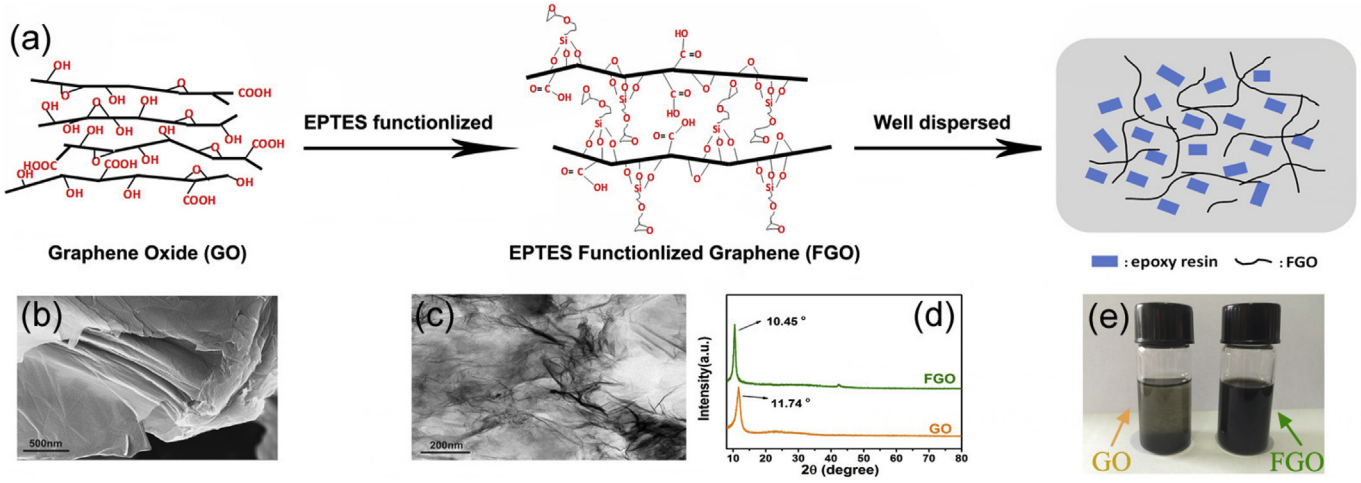

Fig. 1. (a) schematics of EPTES functionlized graphene oxide preparation; (b) SEM image of GO; (c) TEM image of FGO dispersed in n-butyl alcohol& epoxy solution; (d) the wide-angle X-ray diffraction (XRD) patterns of GO and FGO; (e) photographs of GO and FGO dispersion in epoxy matrix. All the photographs were taken three weeks after their preparation. (A color version of this figure can be viewed online.)