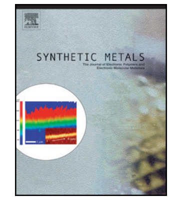
Synthetic Metals 212 (2016) 186–194

Contents lists available at ScienceDirect

Synthetic Metals

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



Fabrication study of a new anticorrosion coating based on supramolecular nanocontainer

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ARTICLE INFO

Article history:
Received 30 August 2015
Received in revised form 22 October 2015
Accepted 27 October 2015
Available online 23 November 2015

Keywords:
Multi-walled carbon nanotubes
β-cyclodextrin
Release
Corrosion inhibitor

ABSTRACT

A new type of functional nanoreservoir based on multi-walled carbon nanotubes (MWCNTs) and β-cyclodextrin was synthesized through a new and facile chemical method. The functional nanoreservoir (β-cyclodextrin/MWCNTs) loaded with a "green" corrosion inhibitor benzimidazole (BZ) was admixed into epoxy as a filler to enhance its anticorrosion performance. The structure and morphology of nanoreservoir were studied by SEM, TEM, XRD, BET analyses, FT-IR, ^{1}H NMR, and TGA. The anticorrosion and self-healing properties of coating were investigated by electrochemical impedance spectroscopy (EIS) and scarification test; the studied results indicated that the addition of functional nanoreservoir loaded with the corrosion inhibitor could significantly improve resistance to steel corrosion, which was attributed to the release of the encapsulated corrosion inhibitor.

1. Introduction

Corrosion is a serious problem which could give rise to enormous damage to society and property. Various methods such as cathodic protection, insulating coatings and corrosion inhibitors have been applied to protect metal against corrosion [1–4]. The coating is one of the most available methods for the protection of metal against corrosion. Recently, researchers' attention has been directed to the development of nanocontainers which have the ability to release corrosion inhibitor when the coating is invaded by a corrosion medium.

So "smart" functional coating is one of the most intensively studied coatings, which received considerable attention due to its self-healing property. Encapsulation of corrosion inhibitors within responsive nanocontainers is an alternative promising technology for self-healing protective coating. Many different nanocontainers have been introduced for the encapsulation and controlled release of chemically active agents such as silica nanoparticles [5,6], polymer capsules [7] and polyelectrolyte nanoshells produced by layer-by-layer self-assembly [8,9]. Frederico Maia et al. [10] fabricated a new nanoreservoir based on silica nanocapsules (SiNC) which loaded with the corrosion inhibitor 2-mercapto-benzothiazole (MBT); the results showed a clear dependence of the release profiles on corrosion-relevant triggers such as pH and Cl^- concentration. Mingxing Huang et al. [11] manufactured polyurethane microcapsules containing hexamethylene diisocyanate as core materials via the interfacial polymerization reaction of commercial methylene diphenyldiisocyanate (MDI) prepolymer and 1,4-butanediol in an oil-in-water emulsion, and the results indicated that a significant corrosion retardancy occurred in the self-healing coating under an accelerated corrosion process.

However, most of them only acted as a nanocontainer for the release of a corrosion inhibitor; they could not improve other properties of the coating. Just like natural halloysite clay nanotubes were usually used as nanocontainers for encapsulating the corrosion inhibitor [12–16] and addition of small amounts of halloysite could significantly enhance the tensile properties of the polymer coating [14]. MWCNTs soon became the focus of research scientists due to the superior properties. As fillers, the addition of MWCNTs could enhance the mechanical performance of coating. Chen et al. [17] detailed a flexible method for functionalizing multi-walled carbon nanotubes (MWCNTs) with polyurea (PU) coating using molecular deposition, and demonstrated significant increases in tensile strength and modulus. An et al. [18] reported that carbon nanotubes (CNTs) have been deposited onto carbon-fiber fabric using electrophoretic deposition (EPD) prior to the infusion of epoxy resin for the production of carbon/epoxy composites, and the mechanical properties were significantly improved.

Cyclodextrin (CD) is a cyclic oligosaccharide, which is generated by the CD glucose enzyme in starch. The most commonly used is β-CD, which is composed of seven glucose primitives by 1, 4 sugar

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http://dx.doi.org/10.1016/j.synthmet.2015.10.022
0379-6779/

glycoside key connection of tapered cylinder structure. CDs have a special molecular structure; they are conical with a slightly cylindrical structure. Their external surface is hydrophilic, and the interior is a hydrophobic cavity of a certain size, which renders the CDs their unique "hydrophilic, hydrophobic" properties [19]. They can selectively bind small organic molecules or ions to form inclusion complexes with certain stability. CDs and inclusion complexes are host and guest, respectively [20]. As popularly known, CDs have become an important subject of supramolecular chemistry and have been widely used in areas of analysis and chemical separation, environment protection; also in textile, coating, cosmetic, pharmaceutical, drug-controlled release, and oil-recovery industries [21–25].

To the best of our knowledge, there is no report yet on the nanocontainer composed of multi-walled carbon nanotubes and β-cyclodextrin. Thus, inspired by the above research attributions, an attempt has been made to combine the unique physical and chemical properties of carbon nanotubes and β-cyclodextrin. Herein, we report a new and facile approach to manufacture the nanocontainer (MWCNTs/β-cyclodextrin). Then the nanocontainer, encapsulated with benzimidazole, was added to the epoxy coating, and the inhibition action of the composite coating was also studied by EIS in the 3.5 wt% NaCl solution; the results of EIS showed that the addition of functional nanoreservoir loaded with the corrosion inhibitor could significantly improve resistance to steel corrosion. In this communication, the schematic diagram of the experimental process is given in Scheme 1.

2. Experimental

2.1. Materials and equipments

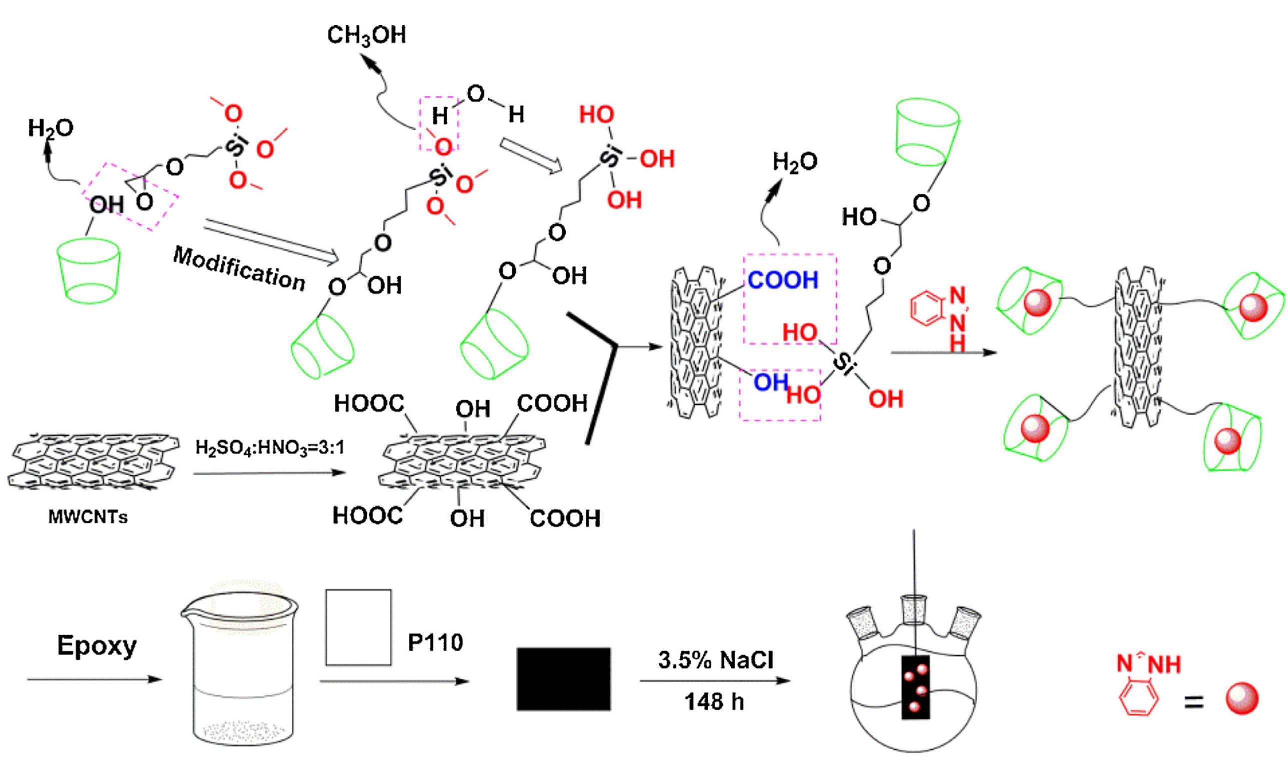
The following reagents used in the experiment were purchased from Kelong Chemical Reagent Factory (Chengdu, China): γ-(2,3-epoxypropoxy) propyltrimethoxysilane (GPTMS), acetone, sulfuric acid, nitric acid, N,N-dimethylformamide (DMF), sodium hydroxide, and acetic acid. The average molecular weight of β-CD was 1134.98 (g/mol). Benzimidazole was obtained from Sigma-Aldrich. Multiwalled carbon nanotubes (MWCNTs) were provided by Chengdu Organic Chemistry Limited Company of Chinese Academy of Sciences. The following equipment were used in the experiment: JSM-7500F (SEM, JEOL, Tokyo, Japan), X'Pert Pro diffractometer (PANalytical, The Netherlands), Bruker Avance III 400 NMR (BrukerBioSpin, Switzerland), numerically controlled ultrasonic cleaners of KQ22OOD model (Kunshan ultrasonic instrument Co., Ltd., China), WQF-520 infrared spectroscopy (Beijing Rayleigh Analytical Instrument Company, Chaoyang, Beijing, China), STA 449 F3 (Netzsch, Germany), JEM-100CX (TEM, JEOL, Tokyo, Japan), and EIS (CS310, Wuhan CorrTest instrument Co., Ltd.).

2.2. Acidification of MWCNTs

MWCNTs were added to mixed acid (concentrated sulfuric acid: concentrated nitric acid = 3:1) and dispersed by ultrasonic cleaners for 30 min. The acidified MWCNTs were poured into a three-necked flask and stirred for 12 h at 40 °C. Then, the mixture was poured into a large amount of deionized water, washed to neutral by sodium hydroxide solution, and dried at 80 °C.

2.3. Synthesis of KH560/β-CD

In a round-bottom flask, 5 g of previously dried β-CD was dissolved in 50 mL of dried DMF at 55 °C under an inert atmosphere, to which 6.0 mL of KH560 was added (corresponding to a β-CD: KH560 molar ratio 1:6). Then, a given mass of sodium hydroxide (0.1 g) was added, and the solution was kept under an inert atmosphere, with vigorous stirring for 48 h, giving rise to γ-(2,3-epoxypropoxy) propyltrimethoxysilane-modified β-CD. Then, the modified β-CD was cooled to room temperature, separated by precipitation using a large amount of acetone, and dried in 45 °C vacuum to obtain the faint yellow powder, which was water-soluble.



Scheme 1. Synthesis of the nanocontainer and preparation of the anticorrosion coating.