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In situ electrochemical synthesis of polyaniline/*f*-MWCNT nanocomposite coatings on mild steel for corrosion protection in 3.5% NaCl solution

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ABSTRACT

Nanostructured composites increase their sensitivity and performance when employed as coating material in corrosive environments. This present study was conducted to elucidate the use of functionalized carbon nanotubes (CNTs) as reinforcement to enhance the corrosion and mechanical behavior of polyaniline (PANI) coatings for the protection of mild steel (MS) structures. Different techniques like Raman spectroscopy, ATR-IR and FESEM analysis were used to evaluate their structure and morphology. FESEM images of the fabricated PANI/*f*-CNT composites suggest excellent dispersion of CNTs in PANI matrix with one-dimensional core–shell structure. PANI/*f*-CNT nanocomposite shows an improvement in the mechanical properties with an increase in the hardness value. Hydrophobic nature of nanocomposite coatings was verified by contact angle measurements. The evaluation of electrochemical corrosion behavior of nanocomposite coated MS was achieved by monitoring the anodic current–potential polarization curves and electrochemical impedance response. Finally, it was concluded that PANI/*f*-CNTs nanocomposite coatings are potentially employed as anticorrosive coatings for mild steel against corrosive environment.

1. Introduction

Polymer nanocomposites have attracted great research and development interests due to their wide applications in batteries, solar cells, sensors and anticorrosion coatings [1–3]. In particular, the preparation of nanocomposites comprising conducting polymers and carbon nanotubes (CNTs) has significantly increased attention in recent years due to the synergistic effects resulting from the combination of these two classes of materials. Among the conducting polymers (CPs), polyaniline (PANI) has occupied the prime position on account of its aqueous solubility, high conductivity, good redox reversibility, swift change of color with potential and good environmental stability. However, the same as other CPs, PANI has poor mechanical stability because of typical shrinkage, breaking, and cracks appearing in aggressive environment, which is connected with volumetric changes of the polymer during charging and discharging. In addition, high porosity is huge concern when PANI is used as the coating material for corrosion protection since the porous structure can facilitate electrolyte uptake and lead to initiate the corrosion at metal coating interfaces. To extend the functions or improving the performances, PANI generally has to be blended with other functional materials to form composites.

Investigation on carbon nanotubes (CNTs) has rapidly grown over the past decade, due to their extraordinary physical and electrical properties. Combining the lightweight, high conductive, thin, porous, and freestanding characters of the CNT network and the unique redox properties of PANI, the PANI/CNT composite film has expected to act as excellent coating materials for corrosion protection applications. Recently, a variety of methods have been reported for constructing composites from the combination of CNTs with conducting polymers [4–6] and the target is to attain an improved synergistic effect in regard to the properties of the two components. Several contrasting theories have been proposed to describe the role of CNTs in corrosion inhibition mechanism of polymer coatings [7].

Gupta and Miura [8] have synthesized composite films of PANI-CNT using the electrochemical deposition method for high performance supercapacitors. Karim et al. [9] demonstrated the complexity of nanotubes coated with PANI. These complex nanotubes had a higher conductivity and thermal stability than PANI but lower than CNT. The drawback of using CNTs is that CNTs are

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difficult to process and insoluble in most solvents. In order to broaden their applications, it is necessary to tailor their solubility properties. Functionalization of CNTs has been attained by an oxidation process, which involves ultrasonic treatment in a mixture of concentrated nitric and sulfuric acid. As a result of this treatment, the ends and sidewalls of the treated CNTs become attached with carboxyl groups. It has also been reported that surface modification of CNTs might intensely affect the morphological and thermal behaviors of the synthesized core–shell CNTs/CP nanocomposites. [10]

Electrochemical polymerization has been proven to be the preferred synthesis route for conducting polymers (CP) and it has also been successfully adopted for the synthesis of classical CNT-CP nanocomposites [11]. To exploit the CNTs effectively as nanofillers for the enhancement of either protective or mechanical properties of the polymer matrix, it is necessary to disperse them uniformly throughout the matrix without damaging their integrity. Uniform dispersion of CNTs in a polymer matrix is the first step in the successful fabrication of polymer/CNT nanocomposites. One of the most promising approaches for synthesizing nanocomposites involves the usage of surfactants to wrap a polymer around the CNTs. Anionic surfactant such as sodium dodecyl sulfate (SDS) is widely employed for the dispersion of CNTs [12] and the addition of SDS also impacts the wetting behavior and interfacial adhesion, which, in return, has an effect on the ability of the surfactant to disperse the nanotubes. Herein, we demonstrate a simple and versatile route for the fabrication of PANI/*f*-CNT nanocomposite coatings via in situ electropolymerisation directly onto the surface of mild steel.

2. Experimental

2.1. Materials

In this present investigation, mild steel (MS) was used as a base substrate and the composition of MS was in wt.%. 0.040 C, 0.350 Mn, 0.022 P, 0.036 S and balance Fe. The MS substrates (size ≈1 cm × 1.5 cm and 0.5 mm thick) were mechanically grinded with different grit size of SiC papers from 400 to 2400. Further, they were degreased with acetone in an ultrasonic bath to remove the impurities, rinsed thoroughly with double distilled water and finally dried in air. Prior to each experiment, the substrates were treated as described and freshly used with no further storage.

Aniline (An), oxalic acid and sodium dodecyl sulfate (SDS) were purchased from Sigma–Aldrich. All the analytical grade chemicals were used as received. Multi-walled carbon nanotubes (MWCNTs) were purchased from Iljin nanotech. The outer and inner diameters of MWCNTs were 10–20 and 5–10 nm, respectively, with lengths in the range of 5–20 μm. Aqueous electrolytes used for the synthesis of the polymer films were prepared using double distilled water. All experiments were carried out at room temperature. Electropolymerization and other electrochemical studies were carried out in a conventional three electrode system with MS substrates as working electrode, high-density graphite as counter electrode and saturated calomel electrode (SCE) as reference electrode and all the potentials in the text were referred to the SCE. Gamry Instrument potentiostat/galvanostat/ZRA (Reference 3000) was used for electropolymerization and other electrochemical studies. Gamry applications include software DC105 for corrosion, EIS300 for EIS measurements, and the Echem Analyst 6.0 software package for data fitting.

2.2. Preparation of functionalized carbon nanotubes (f-CNT)

MWCNTs (2.0 g) were ultrasonicated for 12 h in 200 ml of a mixture of H_2SO_4/HNO_3 (3:1). Then the sample was magnetically stirred at 80 °C for 12 h. The resulting products, the carboxylated CNTs (CNT-COOH), were neutralized to pH 7.0, centrifuged and subsequently washed with deionized water using a dialysis membrane for 24 h. The final carboxylated CNTs (CNT-COOH) were separated by being centrifuged and dried under vacuum at 40 °C.

2.3. Preparation of PANI/f-CNTs composite coatings

Polyaniline/*f*-CNT nanocomposite coatings were electrochemically synthesized by cycling the working electrode potential between −200 and 1200 mV at a scan rate of 50 mV s^{-1} from an aqueous oxalic acid solution containing 0.1 M aniline monomer and 0.01 M SDS with different CNTs feed ratio (1, 3 and 5 mg/L). In a first step, the carboxylated CNTs (*f*-CNTs) were dispersed in water with a dispersant (0.01 M SDS) under ultrasonic condition for 60 min at room temperature to disperse *f*-CNT in solution. PANI/*f*-CNT nanocomposite (PCNT) were prepared after adding certain amount of the *f*-CNTs suspension solution to the electrolyte. Then, the electrolyte solution was stirred for 15 min during which the electrode was immersed. The electro polymerization was performed from a stagnant solution. At the end of the experiment, polymer coated substrates were removed from the polymerization medium and rinsed with deionized water to remove unreacted monomer molecules before being dried in air. The same procedure was used for the synthesis of pure polyaniline coatings on MS substrates.

The thickness of the polymer coatings was measured using an Elcometer instrument. The average thickness of PANI and PCNT coatings was approximately 8.17 μm and 8.51 μm, respectively.

2.4. Characterizations

ATR-IR spectra of the coated MS were recorded in the range of 400–4000 cm^{-1} using IR reflectance spectrophotometry (PerkinElmer, Spectrum One, with universal ATR attachment with a diamond and ZnSe crystal, the Netherlands). Raman spectral analysis was performed using Yvon Jobin Horiba Raman spectrometer with the spectrum window of 200–2000 cm^{-1} through green type laser source at 532 nm. The surface morphology of coated MS was observed using field emission scanning electron microscopy (TESCAN, High Resolution schottky FE-SEM) at an acceleration voltage of 20 kV and irradiation current of 10 μA.

Contact angles of the substrates were determined by contact angle goniometry at 25 °C using an Attension optical goniometer interfaced with image-capture software by injecting a 2 μl liquid drop. Deionized water was used as the test liquid. The standard deviation of contact angle measurements is about ±0.1°. To obtain reliable contact angle data, five droplets were dispensed at different regions of the uncoated and coated MS substrates.

2.5. Mechanical characterization

For the characterization of hardness of the nanocomposite coatings, load–displacement curves for the coatings were measured by a dynamic hardness tester (CSM micro-combi tester.) The indentations were conducted using the load control mode, that is, a loading process was applied to a maximum of 40 mN and then reversed for a preset peak load. The initial load was preset to 0.01 mN and a loading/unloading rate was 2 mN/S. Each measurement was repeated at least five times.

2.6. Electrochemical measurements

Electrochemical studies of uncoated and coated MS substrates were performed in 3.5% NaCl medium by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The anodic and cathodic polarization curves were