



# Effect of functionalization of carbon nanotubes on mechanical and electrochemical behavior of polyaniline nanocomposite coatings



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## ABSTRACT

Functionalization of carbon nanotubes (CNTs) is recognized to enhance their dispersion nature and improves the overall performance of the CNT-polymer nanocomposite. In this current study, effective attempt of constructing nanocomposite comprised of polyaniline (PANI) and functionalized CNTs has been done for the purpose of surface protection of mild steel (MS). The synthesized nanocomposites were investigated in terms of morphology, chemical structure and thermal stability with scanning electron microscope (SEM), attenuated total reflectance infrared (ATR-IR), UV–visible spectral and thermal gravimetric analysis (TGA) methods, respectively. SEM investigations evidenced the uniform fibrous morphology in PANI/CNT nanocomposites with nanometer-sized diameters. TGA curves confirmed the enhanced thermal behavior of PANI with the inclusion of functionalized CNTs. The improved corrosion performance of PANI/CNT nanocomposite in 3.5% NaCl solution was corroborated by electrochemical impedance spectroscopy, electrochemical frequency modulation and potentiodynamic measurements. The origin of such enhanced corrosion protection property is explained from the view point that the interfacial interactions between functionalized CNTs and PANI matrix, greatly improves at the polymer/filler bond stability resulting in a better corrosion performance.

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## 1. Introduction

Pure carbon nanostructures and especially nanotubes exhibit many fascinating features, such as ultrahigh charge carrier mobility, huge thermal conductivity, tremendously large surface area, outstanding mechanical strength, and flexibility, arising from the purely  $sp^2$  hybrid carbon structures [1]. In particular, carbon nanotubes (CNTs) and graphene have attracted much attention as fillers in various types of nanocomposite materials. In particular, CNTs are more favorable additives for polymer materials due to their extraordinary mechanical, electrical, and thermal properties. Recent studies have revealed that CNT/polymer composites can be used for advanced multifunctional applications [2–4]. Although several polymers have been employed as matrix materials in CNT/polymer composites for various targeted applications [5], CNT/conducting polymer structures have been recommended for a wider range of applications [6]. Among the conducting polymers, polyaniline (PANI) is unique and extensively investigated owing to its direct synthetic procedure, environmental constancy, facile processability and, ease of reversible conversion from an insulating to a conducting state via doping and dedoping routes [7–9].

The fabrication of PANI/CNT nanocomposite has expected great attention in recent years, since the incorporation of CNTs into PANI can outcome in novel composite materials with improved properties. For

example, Wallace et al. [10] have reported that the PANI fibers comprising CNTs presented important enhancement in mechanical strength and conductivity. As both PANI and CNTs are outstanding materials for the construction of electrochemical devices [11], the combination of these two materials is also expected to be an admirable platform for corrosion protection applications [12].

By merging the attractive properties of CNTs with PANI, the hybrid nanocomposite provides innovative opportunities, ranging from chemical sensors to molecular electronic devices [13]. However, poor dispersion of CNTs in polymer matrix due to strong intertube interactions can reduce the conversion of the excellent mechanical properties of CNTs into the CNT-filled nanocomposites. The effective utilization of CNTs in composites also depends on their ability to disperse individually and homogeneously within a matrix material. An approach to address this challenge is the covalent or noncovalent functionalization of CNTs to increase their interaction with the polymer matrix leading to enhanced dispersibility.

To date, several chemical functionalization methods have been introduced including covalent side-wall functionalization, noncovalent functionalization and oxidation by nitric acid-etching [14]. It is already reported that the covalently bound oxygen functional groups in CNTs alter the local bonding environment from  $sp^2$  to  $sp^3$  hybrid structures and bring about novel properties [15]. Wu and Lin have proposed that the hydrogen bonding interactions, rather than electrostatic interactions, occur between the amino groups of aniline monomers and the carboxylic acid/acyl chloride groups of functionalized MWCNT together

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with the  $\pi$ - $\pi$  interaction [4]. However, the interaction of functionalized CNTs with polymer matrix is still imprecise phenomenon. Mekki et al. have recently reported that the strong supporting evidence for the effect of aryl diazonium salts in attaining conductive protuberance-free, finely structured PANI shells chained to MWCNTs [16]. However, the carboxylic acid and amino functionalization methods have already been established techniques and proved to be the suitable methods for functionalization of CNTs in large extent. Moreover, if the molecules attached on the wall of the CNTs are very small, their behaviors in their nanocomposite may easily tunable one and fascinated by the polymer chain during nanocomposite formation. Recently, the authors have electrochemically synthesized polypyrrole and PANI nanocomposite with carboxylated CNTs for surface protection of steel substrates [17,18]. In this way, the intention of the present study is to evaluate the effect of functionalization of CNTs on the overall performance of polymer nanocomposite for surface protective coatings. To the best of our knowledge, this report is the first dealing with the mechanical and electrochemical corrosion performance of PANI coatings modified with different functionalized CNTs.

Herein, we deliver the results of the experimental investigation of the effects produced by the carboxylic and amino functionalized CNTs on the corrosion protection performance and mechanical aspects of the resulting PANI/CNT nanocomposites.

## 2. Experimental

### 2.1. Materials

Aniline (An), oxalic acid, sodium dodecyl sulfate (SDS) and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. All the analytical grade chemicals were used as received. Multiwalled 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  $\mu$ m. Aqueous electrolytes used for the synthesis of the polymer films were prepared using double distilled water.

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  $\approx$  1 cm  $\times$  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. 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 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  $^{\circ}C$  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 (c-CNT) were separated by being centrifuged and dried under vacuum at 40  $^{\circ}C$ .

To prepare amino functionalized CNTs (a-CNT), c-CNTs were suspended in  $SOCl_2$ , and the suspension was treated in an ultrasonic bath for 20 min and stirred at 70  $^{\circ}C$  for 36 h. The solid was then separated by filtration and washed with anhydrous tetrahydrofuran. Subsequently,

it was dried under vacuum at 40  $^{\circ}C$  for 12 h, and acyl-chlorinated CNTs (CNT-COCl) were obtained. Further, CNT-COCl was reacted with 50 ml ethylenediamine solution at 100  $^{\circ}C$  for 24 h. After cooling to room temperature, the a-CNTs were washed with ethanol five times to remove excess diamine. Finally, the black solid was dried at room temperature for overnight under vacuum.

### 2.3. Synthesis of PANI/f-CNTs nanocomposites

PANI/f-CNT nanocomposites were synthesized by in situ chemical oxidative polymerization of aniline monomer in the presence of f-CNTs. In a typical synthesis, different f-CNTs (2% wt.) were ultrasonicated in DI water for 2 h to obtain dispersed suspensions. The aniline monomer (3.23 g, 1.0 mol) was slowly added to the f-CNT suspension with constant stirring followed by ultrasonication for 1 h. A precooled (4  $^{\circ}C$ ) aqueous solution of ammonium per sulfate (11.42 g, 1.5 mol) (25 ml) was added drop wise into the aniline/f-CNT mixture under constant stirring. After the addition of oxidant (APS), the reaction mixture was kept under constant stirring for 24 h at 4  $^{\circ}C$ . Finally, the deep green precipitate of PANI/f-CNT nanocomposite was filtered and washed thoroughly with DI water until the filtrate became acid free. The precipitate was dried in a vacuum oven at 60  $^{\circ}C$  for 12 h. The PANI/f-CNT nanocomposite with c-CNTs and a-CNTs are abbreviated as PCNT1 and PCNT2, respectively.

The MS substrates which were previously pretreated in acetone and then, PCNT1 and PCNT2 were coated using dipping method. Appropriate amount of the synthesized polyaniline and nanocomposite samples (10 wt.%) was dissolved in DMSO with continuous stirring for 2 h. This produced a uniform dispersion of PANI in the DMSO solution with no settling. In order to apply an equal coating thickness on the MS substrates, the time of dipping in coating bath was similar for all the synthesis conditions. The duration of dipping process was 1 min (including immersing and eliciting). Subsequently, the coated substrates were dried in oven at the temperature of 60  $^{\circ}C$  for 18 h.

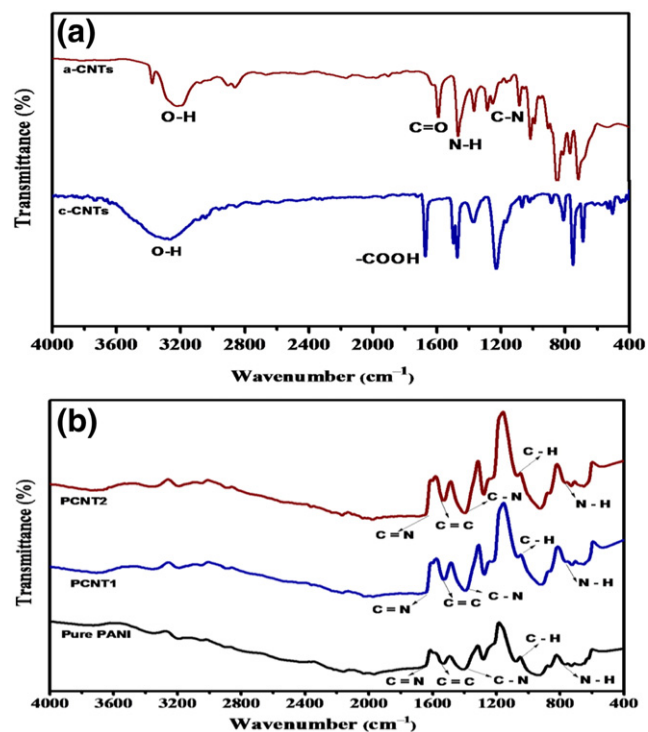


Fig. 1. (a) IR curves of a-CNTs and c-CNTs (b) IR curves of synthesized PANI, PCNT1 and PCNT2 samples.

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