



# Synthesis of conductive polyaniline–graphite nanocomposite in supercritical CO<sub>2</sub> and its application in zinc-rich epoxy primer



E. Akbarinezhad\*

Coating Research Group, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-1998, Tehran, Iran

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## ABSTRACT

Exfoliated polyaniline–graphite (PAniG) nanocomposite (NC) with high electrical conductivity was synthesized via in situ polymerization of aniline in the presence of intercalated graphite in ScCO<sub>2</sub> medium. Ammonium peroxydisulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (APS) was used as an oxidizing agent. The morphology and structure of synthesized PAniG NC was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). Synthesized PAniG NC was used to modify the barrier properties and cathodic protection behavior of a commercial zinc rich epoxy primer (c-ZRP) on low carbon steel (CS) substrate. The protective properties of original and modified ZRPs (m-ZRP) were investigated using open circuit potential (OCP) measurements and electrochemical impedance spectroscopy (EIS) method. It was found that after immersing coated CS for 365 days in 3.5% sodium chloride solution the OCP for m-ZRP remained at the cathodic protection region (lower than  $-0.86$  V/SCE), while for c-ZRP it was passed out of protection region after immersing 100 days. EIS analysis revealed that in m-ZRP the zinc consumption and formation of zinc oxide was delayed and after 100 days of immersion, resistance of c-ZRP and m-ZRP reaches to  $2.48 \times 10^4 \Omega$  and  $2.56 \times 10^3 \Omega$ , respectively. Results revealed that the performance of m-ZRP improved due to the barrier properties of PAniG NC which added to the primer.

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## 1. Introduction

During the past decades, many attempts have been made to replace toxic inhibiting pigments which are used in the organic corrosion protective paint coatings [1–5]. Intrinsically conducting polymers (ICPs) have been found to be useful as a new class of environmentally friendly materials to raise corrosion protection of metals [6–9]. Amongst ICPs, polyaniline (PAni) has gained high technical attention due to its good combination of properties such as: the aniline monomer is less expensive than other monomers used for ICPs, the synthesis of PAni is very simple, it has numerous application possibilities, and its properties can be tuned easily. Applications of PAni in many areas such as antistatic and corrosion inhibition coatings [10–12], electrochromic display [13,14], sensors [15,16], light-emitting diodes and capacitors [17,18], and gas permeation membranes [19,20] have been reported.

The application of PAni as an inhibitive coating for corrosion protection of active/passive alloys was reported by DeBerry [21]. Recently, there has been a great interest in using PAni as a

corrosion protective film or pigment to protect steels, and other metals and alloys [22–25]. PAni can be synthesized by chemical oxidative polymerization and then be used as corrosion inhibitive pigment, or it can be deposited on the metallic parts through the electro polymerization of aniline. Application of PAni in combination with other inhibitive pigments is of great interest during these years [26–30]. Recently Meroufel et al. [31] have reported the addition of polyaniline into a zinc rich primer (ZRP) in order to enhance the electronic conduction paths between zinc particles inside the coating and the steel substrate. Armelin et al. [32] tried to decrease zinc dust content in an epoxy coating from 79 wt.% to 60 wt.% by adding 0.3 wt.% of polyaniline emeraldine salt.

Although PAni has a great potential to be used in ZRPs, but its low electrical conductivity and pH dependency of its conductivity make great challenges for this application. Electrical conductivity of PAni is extremely affected by degree of protonation. Deprotonation of PAni lowers its conductivity from  $4.4$  to  $6.0 \times 10^{-11}$  S cm<sup>-1</sup> [33]. Therefore, development of PAni with improving electrical conductivity is a challenging topic. Electrical conductivity of PAni could be affected by its molecular weight, percentage of crystallinity oxidation level and the properties of used dopants [34]. Among different forms of PAni including: fully reduced non-protonated form (leucoemeraldine base: LB); partially oxidized base form (emeraldine

\* Tel.: +98 21 48255221; fax: +98 21 48255231.

E-mail addresses: [akbarinezhade@ripi.ir](mailto:akbarinezhade@ripi.ir), [akbarinezhad@yahoo.com](mailto:akbarinezhad@yahoo.com)

**Table 1**  
Some properties of c-ZRP and m-ZRPs formula and resulted film.

Character	Standard method	Original ZRP	Modified ZRP
Zinc content in dry film (wt.%)	ASTM D2371-85	80.3	0
PAniG content in dry film (wt.%)	–	79.3	1
Dry film thickness ( $\mu\text{m}$ )	ASTM D7091-05	$100 \pm 10 \mu\text{m}$	$100 \pm 10 \mu\text{m}$
Adhesion	ASTM D3359-09	5B	5B
Impact resistance (in.lb)	ASTM D2794-93	60	60
MEK rub resistance	ASTM D4752-03	Rating 5 <sup>a</sup>	Rating 5 <sup>a</sup>

<sup>a</sup> No effect on surface; no zinc on cloth after 50 double rubs.

base: EB); and fully oxidized non-protonated form (pernigraniline base: PNB), only emeraldine salt form is electrically conductive [34].

Some properties of PAni such as electrical conductivity, mechanical properties, thermal resistance, and barrier properties can be modified using synthesis of NCs [35–39]. Incorporation of nano clay into the PAni results in significant enhancement in thermal, mechanical and gas barrier properties [40], but it seems that this incorporation leads to decreasing the final electrical conductivity in resulted NC [41,42]. As graphite is conductive filler with excellent electrical conductivity, it is expected that incorporation of graphite nano-platelet into the polymer matrix would lead to improve electrical conductivity of NCs. It is difficult for the polymers to enter interlayer gallery of graphite due to its small gallery spacing ( $C = 0.67 \text{ nm}$ ) [43]. We have previously reported a successful method to prepare exfoliated polyaniline-graphite (PAniG) NCs with high electrical conductivity via in situ polymerization in  $\text{ScCO}_2$  environment [44].

In this contribution we made an attempt to use this NC in the formulation of a commercial zinc rich primer (c-ZRP) to modify its corrosion protection properties. One weight percentage of metallic zinc content in the c-ZRP was replaced by the synthesized PAniG NC and the resulted paint was named as m-ZRP. The modified and unmodified ZRPs were applied on the low carbon steel (CS) substrate and the corrosion protection performances of coated panels were studied using electrochemical impedance spectroscopy (EIS) during 100 days of immersion in 3.5% sodium chloride solution. Besides, open circuit potential (OCP) of carbon steel coated panels was monitored during 365 days of immersion to obtain and monitor the period of cathodic protection.

## 2. Experimental

### 2.1. Materials

Chemical oxidative polymerization of aniline in hydrochloric acid (HCl) with ammonium peroxydisulfate (APS) was carried out to synthesize PAni. Analytical grade of aniline was purchased from Merck and used as a monomer after twice distillation under reduced pressure. Other chemicals were purchased from Merck and used as received.

### 2.2. Synthesis procedure

At first 0.2 g of graphite powder was dispersed in 150 ml aqueous solution, sonicated for 10 min and stored in laboratory conditions overnight to promote interlayer swelling. An autoclave equipped with mechanical stirrer and volume of 1000 ml (Deutsch & Neumann) was used as high pressure reactor. A gentle flow of  $\text{CO}_2$  was purged into the reactor for about 2 min to remove air. The graphite suspension was charged into the reactor. The reactor was pressurized up to 100 bars by liquid  $\text{CO}_2$ , and the temperature was controlled by employing a water bath at about  $35^\circ\text{C}$ . The reactor was remained at this pressure for 2 h and then depressurized rapidly in order to prepare expanded graphite powders. Aniline

hydrochloride (2 g) was added to the suspension. The obtained suspension was charged into the reactor and liquid  $\text{CO}_2$  was injected into the reactor up to 100 bars at  $35^\circ\text{C}$ . APS (6.12 g) was dissolved in 150 ml of distilled water and charged into the reactor rapidly. The reaction was allowed to proceed at 100 bars and  $35^\circ\text{C}$  for 24 h under mechanical stirring (60 rpm). The produced PAniG NC was obtained from the bottom of reactor under high pressure via rapidly venting of  $\text{CO}_2$  through a pressure release valve. The resulted NC was precipitated by adding the reaction mixture into 500 ml of hydrochloric acid aqueous solution (0.2 M), followed by filtering and washing with 50 ml methanol to remove un-reacted monomers, oxidizing agent and by products. The powdery substance was repeatedly washed by hydrochloric acid (0.2 M) aqueous solution, and dried at  $40^\circ\text{C}$  in vacuum for 24 h.

### 2.3. Characterization methods

FTIR spectra of resulted NCs in KBr pellets were recorded in transmission mode on a Bruker IFS-88 FTIR spectrometer to determine its chemical structure. The spectra were collected from 500 to  $4000 \text{ cm}^{-1}$ . Scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) were used to observe the morphology of the resulted NCs. The bulk conductivity of NCs were measured using a potentiostat-galvanostat (model EG&G 273A) by applying two-line-probe method in atmospheric condition. The NC powder was pressed into a disk of 13 mm in diameter and 0.3 mm thick under pressure of 120 bars. Copper paste was used to eliminate the connection resistance.

### 2.4. Paint formulation

The synthesized NC was added into the c-ZRP to prepare m-ZRP. Some properties of c-ZRP and m-ZRPs formula are presented in Table 1. Commercial and modified ZRPs were applied on the blasted carbon steel panels, separately. An air spraying gun was used to apply the paintings. The dry film thickness was adjusted to be  $100 \pm 10 \mu\text{m}$ . The coated panels were stored in laboratory condition for 10 days before evaluations. The corrosion behavior of coated specimens was determined via measuring the open circuit potential (OCP), and impedance characteristics using EIS method in 3.5% sodium chloride solution in several time intervals up to 365 and 100 days, respectively. A cell with three electrodes was used for electrochemical measurements. The cell contained a coated carbon steel specimen as a working electrode (WE), a graphite rod as a counter electrode (CE), and a saturated calomel electrode (SCE) as a reference electrode. EIS measurements were made using a potentiostat-galvanostat Model 273A equipped with a SI 1255 frequency response analyzer. EIS measurements were done by applying a 5 mV perturbation signal to electrochemical cell at open circuit potential. Impedance spectra were collected in frequency ranges of  $10^4 \text{ Hz}$  to  $10^{-2} \text{ Hz}$  (5 points per decade of logf). ZSim3.22 software was used to interpret impedance data.

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