



## A study on corrosion protection of different polyaniline coatings for mild steel



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### ABSTRACT

The emeraldine base and salt (hydrofluoric acid and camphorsulfonic acid doped) forms of polyaniline (PANI) were synthesized and added to be epoxy coating. The corrosion protection of different PANI coatings was studied by EIS. Results indicated that different PANI coatings could offer the corrosion resistance of mild steel. However, the camphorsulfonic acid-doped PANI coating had the best performance in corrosion protection among the four systems under investigation. The corrosion product layer was analyzed by SEM and XPS, indicating that PANI changed the morphology and component of the corrosion product layer. Moreover, the protective mechanism imparted by PANI was discussed.

### 1. Introduction

PANI has been widely studied for a variety of applications in anticorrosion coatings for the past three decades since DeBerry showed in 1984 that the electrochemically deposited polyaniline (PANI) protected stainless steel by anodic protection [1–6]. Until to the present time, two forms of PANI have been the most thoroughly investigated in anticorrosion coatings: these are the non conducting emeraldine base (EB, half-oxidized form) and the conducting emeraldine salt (ES, half-oxidized and protonated form) respectively. Different results of protection were obtained, and different mechanisms were proposed, depending on the metal used, the method of synthesis, the corrosion environments, and the preparation method of coating.

Some findings indicated that the EB form of PANI had an effective protection for steel in NaCl and NaOH solutions. The positive protection effects of the EB form of PANI was possibly due to its good adhesive property toward the metal substrate and the oxidation-reduction (redox) catalytic property [7–11]. However, other studies showed that the EB form of PANI, even with an epoxy topcoat, did not protect steel from the Na<sub>2</sub>SO<sub>4</sub> solution because of poor barrier property and adhesion [12]. Many studies concluded that the EB form of PANI coating provided better protection from corrosion for steel substrates than the ES form of PANI coating [13]. Nevertheless, an increasing number of researchers revealed that the ES form of PANI coating could provide

protection for different metals [14–17]. Our previous work found that the ES form of PANI coating had better corrosion protection on the surface of magnesium alloy than that of the EB form of PANI coating [18]. In addition, other reports found that the corrosion protection provided by the ES form of PANI coating was strongly influenced by the type of dopant [19].

Moreover, different protection mechanisms of PANI coating, such as anodic protection, barrier protection, corrosion inhibitors, and shift of electrochemical interface, have been proposed [20,21]. The anodic protection of PANI coating is evidenced by the widely observed shift in the corrosion potential to the passive region and increase in the polarization resistance for metal [22,23]. Evidence suggests the formation of a thin oxide layer at the interface between the metal and the coating, offering further protection for metal [24–26]. Some works also reported that PANI/epoxy coating works as a better barrier against the diffusion of the electrolyte and aggressive ions than epoxy coating alone [15]. The study about dopants or counter-ions suggested that PANI can release anions when damage occurs to the coating, forming a second physical barrier that counteracts penetration of aggressive ions [27]. The work suggested that the active corrosion protection action of a conductive PANI form due to shift of electrochemical interface and separation of partial cathodic and anodic corrosion processes [28].

The abovementioned divergent research results and complex mechanism of PANI coating are complicated by many factors that possibly

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influence occurrence of the processes. These results of existing research inspired us to further investigate the corrosion performance and protection mechanism of PANI coating in more detail. Our previous work found that a hydrofluoric acid-doped form of PANI coating exhibited enhanced corrosion protection for magnesium alloy [18]; however, whether it has the same protection for steel is still unknown. Dopants in PANI can play an important role in corrosion protection because of the formation of a metal-dopant interface [15]. José et al. [29] reported that iron cations form a passivating complex with the PANI doping-anion (camphorsulfonate) that acts as a second physical barrier to avoid penetrating aggressive ions in sulfuric acid solutions with or without chloride ions. The question is if Fe-sulfonate could form and have an important role for steel in 3.5 wt.%. Therefore, the EB and ES (hydrofluoric acid and camphorsulfonic acid doped) forms of PANI were selected in this study. Epoxy coatings containing different forms of PANI powders were prepared on the surface of mild steel. The corrosion performances of the prepared PANI coatings in 3.5 wt.% NaCl were then investigated. The protective mechanism of the coatings was also discussed.

## 2. Experimental

### 2.1. Sample preparation

The coating substrate materials were mild steel plates, which were cut into the size of 50 mm × 50 mm × 5 mm. The elemental compositions of these materials are displayed in Table 1. The samples were ground to 400-grit finish, degreased in acetone and ethanol, and dried in air before the experiment.

The EB, hydrofluoric acid-doped, and camphorsulfonic acid-doped form of PANI powders were synthesized by chemical oxidative polymerization in the laboratory as described in our previous study [18]. Briefly, some anilines dissolved in hydrochloric acid (or hydrofluoric or camphorsulfonic acid) solution were oxidized and polymerized through dropwise addition of ammonium persulfate solution with constant stirring. After complete polymerization, the dark-green colored polymer powders were filtered and washed with distilled water. The hydrofluoric acid-doped camphorsulfonic acid-doped forms of PANI powders were obtained after further vacuum drying. Especially, the obtained hydrochloric acid-doped powders were dedoped by stirring in aqueous ammonia solution. After the dedoping procedure, the EB form of PANI powders was filtered and washed repeatedly with distilled water and dried in a vacuum. The size of the powder was approximately 5–10 μm.

The different PANI coatings were obtained by dispersing the EB, hydrofluoric acid-doped, and camphorsulfonic acid-doped forms of PANI powders in epoxy resin (E44) using a ball grinding mill. The powder concentration was 10 mass%. Polyamide (651) was used as the curing agent. Epoxy resin and polyamide were obtained from Blue Star Company (China). The coatings were cured at room temperature for 24 h, and then at 60 °C for another 24 h. The thickness of the dry coatings was 100 ± 5 μm, as determined with a PosiTector 6000 coating thickness gauge (DeFelsko Corporation, USA). Epoxy resin without any additions (varnish coating) was used as reference specimens. In this study, EP, EB, HF, and CSA coatings were used to express the varnish and epoxy coating containing EB, hydrofluoric acid-doped, and camphorsulfonic acid-doped form of PANI powders.

**Table 1**  
Elemental composition (wt.%) of mild steel.

C	Mn	Si	S	P	Fe
0.14–0.22	0.30–0.65	≤0.3	≤0.05	≤0.045	Bal

### 2.2. Measurements

The fourier transformation infrared (FTIR) spectroscopy (Nicolet IR200, USA) using KBr pellets was conducted to characterize the synthesized composite powders.

Electrochemical impedance spectroscopy (EIS) measurements were performed at the 100 kHz to 10 mHz frequency range and an the AC amplitude of 20 mV using an Autolab PGSTAT302 potentiostat (Netherlands). A 3.5 wt.% NaCl solution was used as the electrolyte. The coated mild steel, which had an exposed area of 9.8 cm<sup>2</sup>, was used as the working electrode. Pt and a saturated Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. The experimental data were analyzed using the <sup>®</sup>ZsimpWin commercial software (Princeton Applied Research, TN, USA).

After immersion measurement, the coatings on the surface of mild steel were removed. The corrosion morphology of mild steel was characterized with a camera and SEM (JSM-6480).

The surface composition of mild steel was characterized by XPS which was performed with a PHI 5700 ESCA spectrometer using the Al K $\alpha$  X-ray source. The calibration of the binding energy of the spectra was performed with the C 1s (284.6 eV) peak.

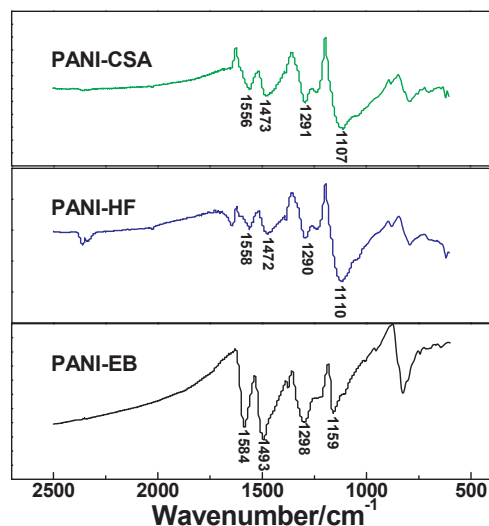
The glass transition ( $T_g$ ) of the coatings was obtained by DSC using TA Q200 (USA). The coatings were heated from ambient temperature to 150 °C at a constant speed (10 °C/min).

## 3. Result

### 3.1. Characterization of the PANI powders

The FTIR spectra of EB, hydrofluoric acid, and camphorsulfonic-acid doped form of PANI powders are illustrated in Fig. 1. For the FTIR absorption spectroscopy of the EB forms of PANI, the vibration at 1584 cm<sup>-1</sup> was for the quinoid rings, with peaks at 1493 cm<sup>-1</sup> attributed to benzenoid ring units [30–32]; the peaks at 1298 cm<sup>-1</sup> correspond to the C–N stretching of a secondary aromatic amine; the peaks at 1159 cm<sup>-1</sup> are assigned to vibrations associated with the C–H of N=Q=N (Q was the quinoid rings). These results showed that the synthesized powder was PANI in emeraldine state [33,34].

The FTIR spectra of hydrofluoric acid or camphorsulfonic acid-doped form of PANI powders show that the characteristic peaks of the EB form of PANI were found to shift to lower wavenumber side because of the addition of hydrofluoric or camphorsulfonic acid. For example, the corresponding peaks of quinoid ring structures were shifted from 1584 and 1159 cm<sup>-1</sup> to 1558 and 1110 cm<sup>-1</sup> (hydrofluoric acid



**Fig. 1.** FT-IR spectra of synthesized polyaniline.

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