

# Electrospinning of polyaniline microfibers for anticorrosion coatings: An avenue of enhancing anticorrosion behaviors



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## ARTICLE INFO

### Article history:

Received 27 October 2015

Accepted 8 December 2015

Available online 18 December 2015

### Keywords:

Electrospinning

Polyaniline

Anticorrosion coating

Microfiber

## ABSTRACT

The pursuit of efficient anticorrosion coatings containing polyaniline (PANI) has been a persistent objective. We present here the experimental realization of PANI microfibers by a simple electrospinning strategy. The resultant anticorrosion coating at an optimal PANI dosage of 25 wt% shows an impressive anticorrosion efficiency of 99.96% even after 20-days test in 0.1 M H<sub>2</sub>SO<sub>4</sub>. The elevated anticorrosion behavior may be attributed to the compact morphology of PANI/poly(methyl methacrylate) microfiber coating. The current study on PANI microfibers provides a new approach of enhancing anticorrosion behaviors of anticorrosion coatings.

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## 1. Introduction

For metallic materials, corrosion reactions have been inevitable natural processes [1–3]. Great achievements have been obtained to prevent or at least weaken the corrosion processes. One of the promising strategies is the utilization of barrier coatings [4,5]. Recently, an arising technique of employing conducting polymers has attracted extensive attentions in corrosion inhibitors for metals [6–8]. Among known conducting polymers, polyaniline (PANI) has a high place because of its high electrical conductivity, good environmental stability, the relatively low cost and its reversible doping–dedoping–redoping chemistry [9–11]. More importantly, PANI played not only physical barrier but also electrochemical protection effects, allowing for potential anticorrosive coatings on metallic substrates [12,13]. These promising performances are attributed to the elevation of the corrosion potential along with a protective passivation layer from redox properties of PANI [14–16]. Hür et al. [17] and Yao et al. [18] have launched studies of utilizing PANI nanofibers as anticorrosion coatings for carbon steels in NaCl solution (3.5 wt%). One of the crucial issues for drop-casting fabricated PANI nanofiber coatings is that the uniformity and poor adhesiveness of the PANI nanofibers coatings limit the further enhancement of anticorrosion

properties [19]. In this fashion, a prerequisite of synthesizing highly efficient anticorrosion coatings is to homogeneously disperse PANI nano/microstructures in coatings. Electrospinning has been recognized as a considerable technique in the fabrication of micro- or nanoscaled conductive polymer fibers [20–30]. For example, MacDiarmid et al. [27] prepared PANI electrospun fibers by using the mixture of PANI–H<sub>2</sub>SO<sub>4</sub> and commonly used polymers such as poly(ethylene oxide), polystyrene, polycaprolactone or polyacrylonitrile [28]. A remaining but important issue is the inherently poor solubility of PANI in the used solvents, making it difficult for PANI to disperse uniformly in the polymeric matrix.

In the current work, we launch a study on electrospinning PANI microfibers blended with poly(methyl methacrylate) (PMMA) in tetrahydrofuran. The resultant PANI fluid was doped with dodecyl benzenesulfonic acid (DBSA) and 10-camphorsulfonic acid (CSA). Our focus is placed on the systematic studies of anticorrosion behavior evolution when used as anticorrosion coatings of Q235 carbon steel.

## 2. Experimental

### 2.1. Reagents and materials

A 3 mm thick Q235 carbon steel sheet [nominal composition (%): C 0.18, Mn 0.45, Si 0.02, S 0.02, P 0.01, and Fe balance] was obtained from Shengxin Science and Technology Ltd. (Yangxin, China). Polymethyl methacrylate (PMMA), aniline, ammonium persulfate (APS), hydrochloric acid (37%), ammonium hydroxide, camphorsulfonic acid (CSA), *m*-cresol, dodecylbenzene sulfonic

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acid (DBSA), sulfuric acid, tetrahydrofuran (THF), anhydrous ethanol and chloroform were purchased from National Medicine Chemicals (China). Aniline monomer was distilled under reduced pressure before use. And other reagents were used as received without further purification.

## 2.2. Preparation of emeraldine PANI (EB)

According to the literature [31,32], aniline (30 mmol) was ultrasonicated in 25 mL of deionized water. 25 mL of hydrochloric acid (2%, w/w) was added to the above mixture with continuous stirring. Thereafter, 25 mL of APS solution (1 M) was added by dropwise for 2 h. Then the mixture was vigorously stirred in ice bath for 3 h. The product was filtered and washed with deionized water and ethanol, respectively. The obtained products were allowed to dry in a vacuum oven at 60 °C afterwards. The resultant HCl doped PANI was converted into EB after being added to 3 wt%  $\text{NH}_4\text{OH}$  for about 6 h under vigorous stirring, washed with deionized water and ethanol, and subsequently dried in a vacuum oven at 60 °C.

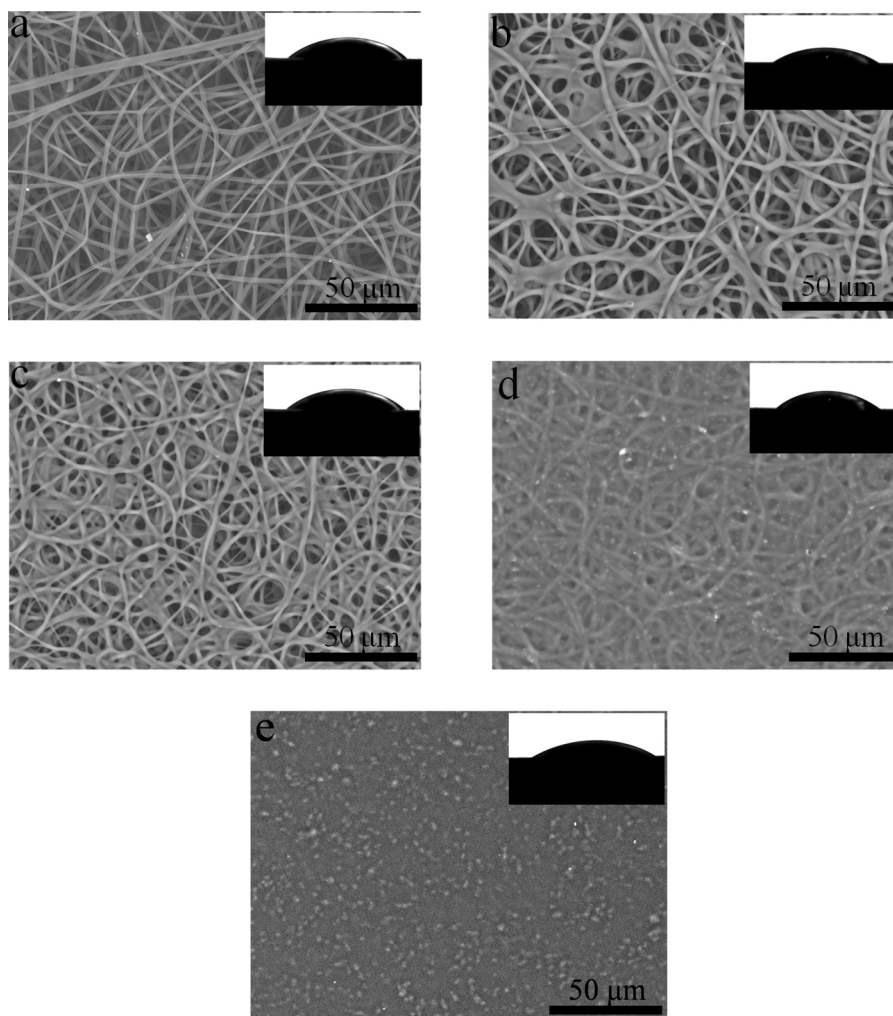
## 2.3. Preparation of CSA and DBSA doped PANI

Refer to the report [33], EB (0.064 g) were dispersed in 25 mL of chloroform with DBSA (0.160 g) under ultrasonic condition for 24 h.

After that, 0.031 g of EB was dispersed by stirring in 2.17 mL solution already containing *m*-cresol and CSA (0.062 g) at 80 °C for 5 h. Eventually, the above two liquids were ultrasonicated for 0.5 h to obtain soluble PANI.

## 2.4. Preparation of PANI/PMMA coatings

Electro-spun solution was obtained by mixing PANI solution and PMMA solution ( $200 \text{ g L}^{-1}$ ) in THF under stirring for 2 h. The PANI/PMMA blends with various PANI dosages (4–35 wt%) were prepared. The as-prepared PANI/PMMA solution was loaded to a 5 mL syringe. A high direct voltage source (Tianjin Dongwen High-voltage Source Plant, DW-P303-1ACF0) was connected to the needle of the syringe and the operation voltage was kept at 12 kV. In this experiment, the syringe whose needle had a diameter of 0.5 cm contained an attached copper wire which was used as the positive electrode. The Q235 carbon steel electrode was used as a collector and the distance between the needle tip and the collector kept 16 cm. The non-woven, fibrous PANI/PMMA mats with a thickness of 40–48  $\mu\text{m}$  were formed owing to the deposition of continuous nanofibers on the Q235 carbon steel. As a reference, traditional PANI/PMMA coatings on the Q235 carbon steel were prepared by a drop-casting technique.



**Fig. 1.** SEM images and static water contact angles of the electrospun PANI/PMMA coatings with various PANI dosages: (a) 4%; (b) 8%; (c) 15%; (d) 25%; (e) 35%.

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