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Facile Preparation of Polyaniline Nanoparticles and Their Dispersion for Waterborne Anticorrosion Coatings

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Waterborne conductive polyaniline/polyvinylpyrrolidone (PANI/PVP) nanoparticles were prepared using as PVP stabilizer and phosphoric acid as dopant via dispersion polymerization. The resulting PANI/PVP nanoparticles were characterized by TEM, FTIR, UV-vis spectra, cyclic voltammetry and XPS, which showed regular spherical morphology with uniform diameters in the range of 60-80 nm and good electroactivity. The addition of PANI/PVP nanoparticles significantly improved the anticorrosion properties of waterborne epoxy coating, based on polarization curves and EIS measurements performed in 3.5% NaCl solution. Especially, the epoxy coating containing 1.0 wt% PANI/PVP exhibited best corrosion protective effect. The remarkably enhanced anticorrosion performance could be attributed to the redox catalytic properties of PANI/PVP nanoparticles and the inhibitory effect of doping anions.

Keywords: polyaniline nanoparticles; waterborne coatings; corrosion; EIS; Tafel curves

1. INTRODUCTION

Since Deberry first reported the polyaniline (PANI) film deposited on stainless surface could significantly reduce the corrosion rate of stainless in sulfuric acid solution in 1985 [1], PANI has attracted a great deal of attention as a new type of anticorrosive coatings [2, 3]. More importantly, many works indicated that PANI can protect various metallic materials such as stainless, iron, copper, zinc and aluminum against corrosion in saline and acid media [4-6]. The corrosion protection mechanism of metal by PANI coatings has been extensively studied, mainly focusing on anodic protection, dopant anions inhibition, barrier protection and shift of electrochemical interfaces [7, 8]. However, PANI coating has some disadvantages such as poor mechanical properties and adhesion, and easy to form defects, which make it difficult to be used alone.

An alternative strategy is adding PANI dispersions into the polymeric resins to form composite anticorrosive coatings. Solvent-based PANI anticorrosive coatings have been commercialized in many countries, which, however, would be replaced for eco-friendly water-based system due to the ever-increasing environmental consideration [9]. Kalendova et al. prepared waterborne PANI anticorrosive coatings by dispersing PANI in epoxy system [10]. However, poor dispersibility and high volume fraction of PANI make this waterborne coating less effective on the metal corrosion protection [10]. It also has been reported that PANI particles with large size and high volume fraction could destroy the mechanical properties of coatings and promote the permeability of H_2O and O_2 molecules [8]. Therefore, improving the water-dispersibility of PANI is necessary to obtain waterborne coatings with high anticorrosive performance. Various methods have been reported to improve the solubility of PANI, including self-doping, counter-ion induced and template polymerization [9]. Among them, the template polymerization is a well-known approach to prepare stable aqueous dispersion of PANI, in which water-soluble polyvinylpyrrolidone [11, 12], poly(vinyl alcohol) [12] or poly(vinyl ether) [13] was used as a template and stabilizer. However, the hydrophilic groups of these stabilizers might decrease the anticorrosion performance of PANI.

Phosphate compound could form a dense phosphating film and improve the adhesion and flash-rust resistance on the surface of metal, which hence can be employed as a corrosion inhibitor [14, 15]. Furthermore, it has been proved that phosphate doped PANI has excellent anticorrosion ability [16]. Chen et al. prepared waterborne conductive PANI nanoparticles by using partially phosphorylated poly(vinyl alcohol) as a codopant and stabilizer, which was then added into aqueous epoxy system to get waterborne coatings with high corrosion protection ability [8]. Wang et al. prepared a waterborne PANI anticorrosive coating, where PANI was doped with phosphate containing ethylene units and waterborne epoxy system was used as matrix [17]. The as-prepared PANI coating exhibited better anticorrosive performance than pure epoxy coating.

In this paper, we prepared waterborne phosphoric acid-doped conductive PANI nanoparticles via dispersion polymerization using polyvinylpyrrolidone as stabilizer. Facile dispersion of PANI nanoparticles into waterborne epoxy coating was achieved. The anticorrosive behavior of the epoxy coatings with various PANI contents was evaluated by Tafel polarization curves and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL

2.1 Materials

Aniline, ammonium persulfate (APS) and phosphoric acid (H_3PO_4, 85%) were purchased from Aladdin (Shanghai, China). Polyvinylpyrrolidone (PVP) was supplied by JH Nanhang Industrial Co., Ltd. Epoxy resin (E51, epoxy value: 0.5, solid content: 98%) and waterborne curing agent (solid content: 60%) were provided by Hangzhou Hanma Coatings & Glass Co., Ltd. The Q235 carbon steel was abraded with 800 and 1,500 SiC paper, and then degreased in acetone by ultrasonication.

2.2 Synthesis of the PANI/PVP nanoparticles

Aniline (2 mL) was added into PVP aqueous solution (4.06 g PVP, 60 mL water) at room temperature. Ammonium persulfate (2.04 g) in aqueous H_3PO_4 solution (1.0 M, 50 mL) was added dropwise into the aniline/PVP aqueous solution for 1 h at -5 °C in an ice-salt bath with vigorous stirring. The reaction was conducted in air for 5 h. The reaction mixture was centrifuged at 5000 rpm for 15 min. The isolated slurry was redispersed in water (10 mL). This process was repeated three times. Finally, the solid was redispersed in water.

2.3 Typical procedure for preparation of waterborne epoxy coating with 1wt% PANI/PVP nanoparticles

5 mL of the aqueous dispersed PANI/PVP nanoparticles (35 mg/mL) obtained above was added to waterborne epoxy curing agent (14.5 g). After being vigorously stirred for 10 min, epoxy resin (10 g) was added. The liquid mixture was stirred for another 30 min, which then was coated on the Q235 carbon steel electrode surfaces. The specimens were dried in room temperature for 7 d. The thickness of coating was 25±2 μm.

2.4 Characterizations

UV-vis spectra were recorded using a UV-vis spectrometer (Lambda 950, Perkin-Elmer). FTIR spectra were conducted on a spectrometer (NICOLET 6700, Thermo) by collecting 32 scans with a spectral resolution of 4 cm^{-1}. Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microscope (FEI Quanta 250 FEG, US) under a vacuum environment, with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded on a TEM instrument (JEOL JEM2100) operated under an acceleration voltage of 200 keV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS UTLTRA DLD spectrometer equipped with an Al Kα radiation. All core-level spectra were referenced to the neutral C_{1s} peak at a binding energy of 284.6 eV.

To evaluate the influence of PANI/PVP on the corrosion performance of waterborne epoxy coating on Q235 steel substrate, EIS and polarization curves were carried out using CHI-660E electrochemical workstation. The test system consisted of a classic three-electrode system in 3.5% NaCl solution at room temperature, wherein a Pt electrode, a saturated calomel electrode (SCE) and a coated Q235 steel (1 cm^2 area) were used as a counter, reference and working electrode, respectively. Before test, the coating/steel system was allowed to attain equilibrium under open circuit potential (OCP) in 3.5% NaCl solution for 1.5 h, then the EIS spectra were recorded in 10^{-2}-10^5 Hz frequency range using 15 mV perturbation potential. Polarization curves were conducted at 0.5 mV/s scan rate by sweeping the potential between ± 200 mV vs. OCP. Cyclic voltammetry was performed in 1 M HCl solution at 20 mV/s scan rate.

3. RESULTS AND DISCUSSION

3.1 Preparation and characterizations of the PANI/PVP nanoparticles

The PANI/PVP aqueous dispersion was prepared via dispersion polymerization using PVP as stabilizer and phosphoric acid as doping agent. The morphology and size of the PANI/PVP nanoparticles were characterized by SEM and TEM, as shown in Figure 1. It was observed that the PANI/PVP nanoparticles showed regular spherical morphology with uniform diameters in 60-80 nm, which is in the range of PANI particle size effectively preventing metal corrosion reported by Wessling [18]. Moreover, FTIR, UV-vis and cyclic voltammetry were used to characterize the structure and electrochemical properties of the PANI/PVP nanoparticles.

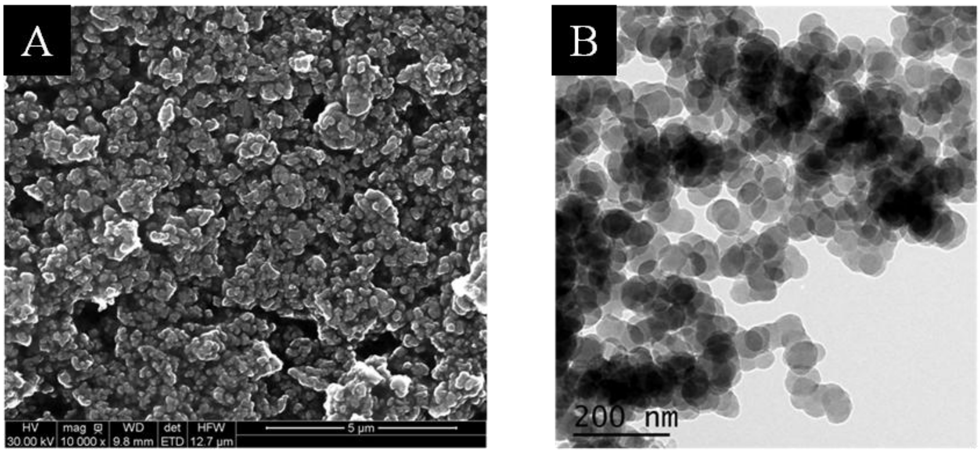

Figure 1. SEM (A) and TEM (B) images of the PANI/PVP nanoparticles.

Figure 2 shows the FTIR spectrum of the PANI/PVP nanoparticles. The two bands at 1565 and 1482 cm^{-1} are assigned to quinoid and benzenoid ring stretching in PANI, respectively [19]. The absorption peaks at 1664 and 1289 cm^{-1} are assigned to C=O and C-N stretching in PVP, respectively [20]. The results indicated that the PVP as a stabilizer existed on the surface of the PANI particles, making the PANI aqueous dispersion stable. Figure 3 displays the UV-vis spectrum of the PANI/PVP nanoparticles. The two adsorption peaks at 324 and 633 nm are ascribed to the π-π^* transition of benzene ring and the benzenoid to quinoid excition transition [21], while the small shoulder peak at 430 nm was the polaron band [19].

The electroactivity of the PANI/PVP nanoparticles was studied by cyclic voltammetry, as shown in Figure 4. The PANI/PVP showed only a redox peak at 0.62 V, which can be ascribed to the transition from a leucoemeraldine base to a emeraldine base [21]. Furthermore, the surface elements of the PANI/PVP nanoparticles were analyzed by XPS spectrum. C_{1s}, N_{1s}, O_{1s} signals can be clearly observed, which were attributed to PVP and PANI. Small P_{2p} signal also was detected, indicating that H_3PO_4 molecules had partly doped the PANI particles. It has been reported that the PANI doped by phosphate compounds was very effective in metal corrosion protection [8, 16, 22]. Moreover, the PANI/PVP aqueous dispersion can easily incorporated into waterborne epoxy coatings. Therefore, it is conceivable that the waterborne PANI containing epoxy coating would probably exhibit improved anticorrosive properties compared with pure epoxy coating, as discussed in the following sections.

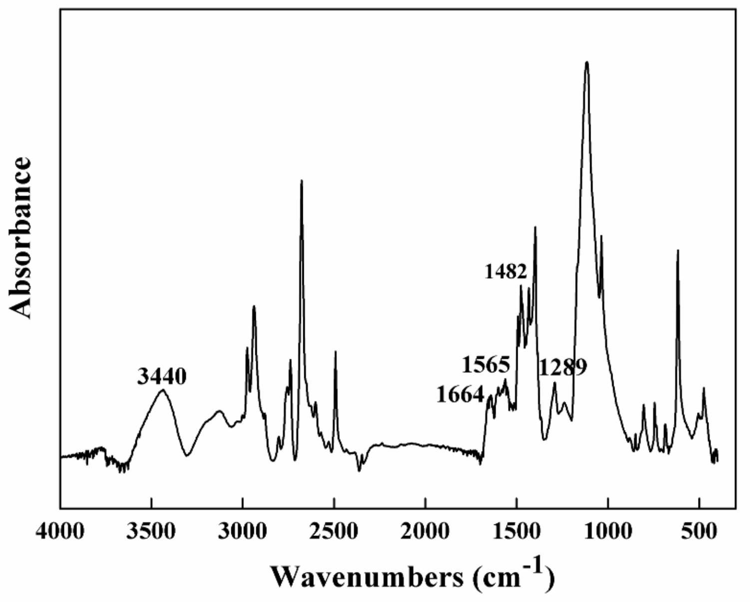

Figure 2. FTIR spectrum of the PANI/PVP nanoparticles.

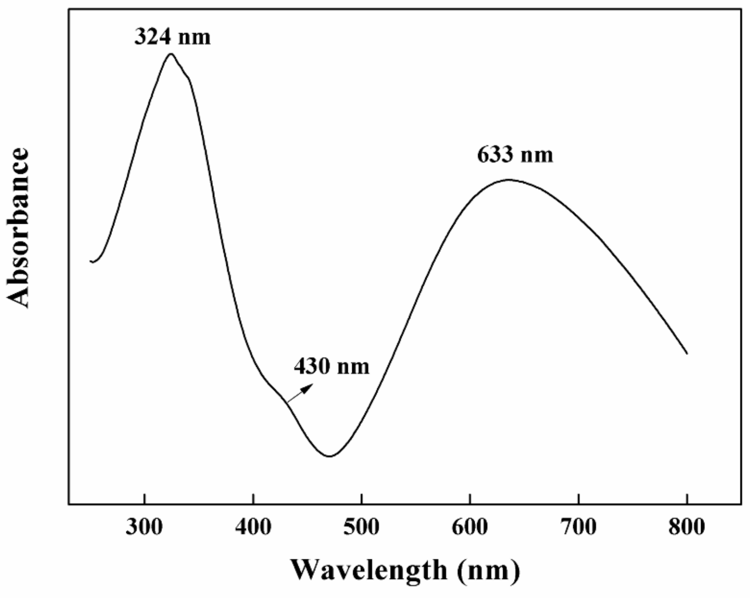

Figure 3. UV-vis spectrum of the PANI/PVP nanoparticles.

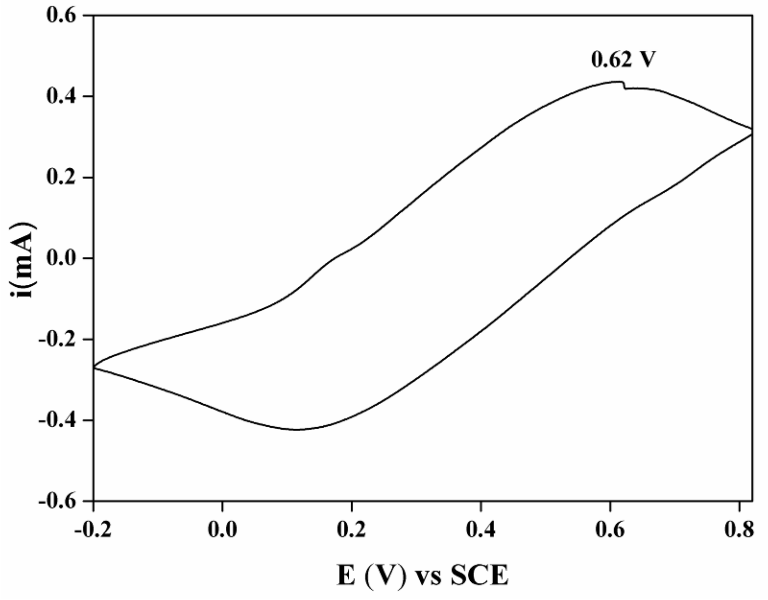

Figure 4. Cyclic voltammogram of the PANI/PVP nanoparticles.

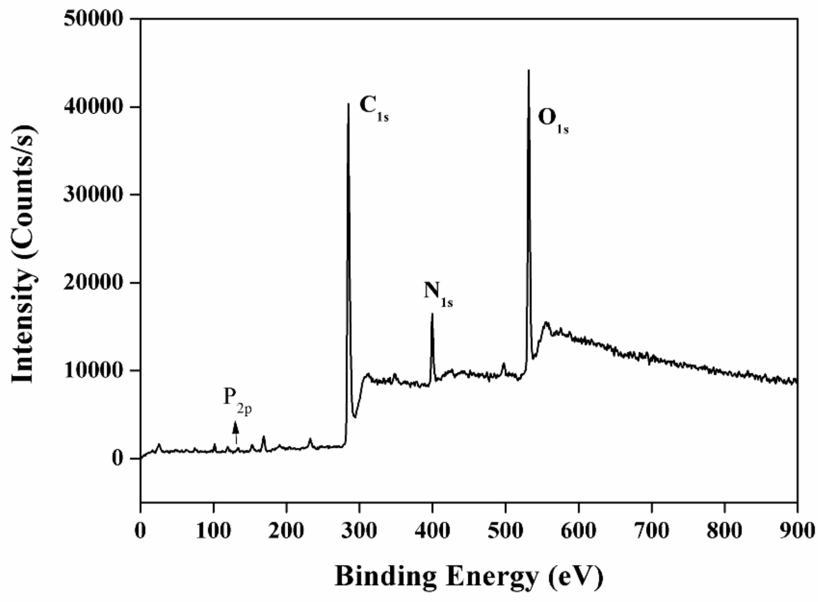

Figure 5. XPS spectrum of the PANI/PVP nanoparticles surface.

3.2 Preparation and morphologies of waterborne epoxy coatings containing PANI/PVP

Waterborne epoxy coatings containing PANI/PVP were obtained by adding PANI/PVP aqueous dispersion into two-component waterborne epoxy resin. In order to study dispersion capability of PANI/PVP in waterborne epoxy coating, SEM was used to observe the fracture surface of composite coatings, as shown in Figure 6. The PANI/PVP containing epoxy coating displayed relatively smooth fracture surface. Moreover, the PANI/PVP nanoparticles were uniformly dispersed in epoxy coating, which would probably improve corrosion protect performance of epoxy coating.

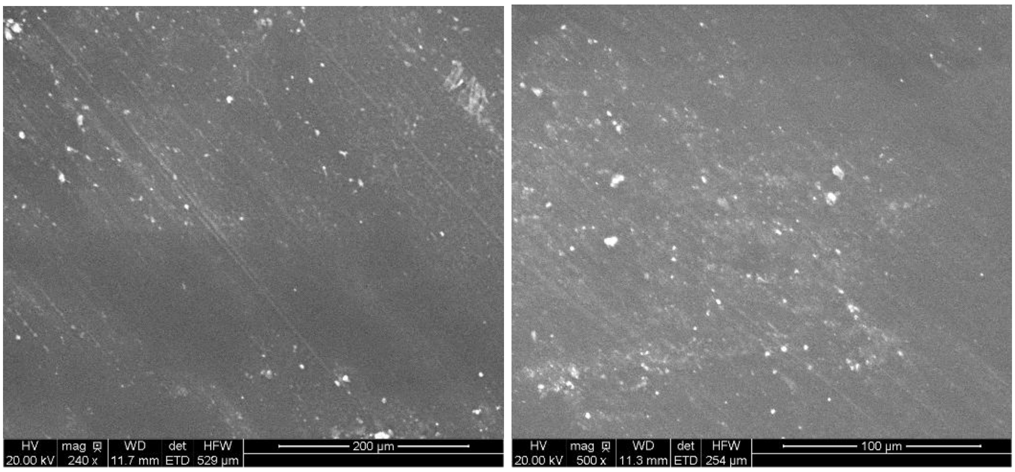

Figure 6. SEM images of fracture surface of PANI/PVP modified epoxy coating. left: ×240 times; right: ×500 times.

3.3 Anticorrosive properties of waterborne PANI/PVP containing epoxy coatings

To evaluate the anticorrosive properties of waterborne epoxy coatings containing different PANI/PVP content, polarization curves and EIS were used to investigate the corrosion behavior of composite coatings. Figure 7 depicts the Tafel polarization curves of neat waterborne epoxy coating (EP), 0.5% PANI/PVP-EP, 1.0% PANI/PVP-EP and 2.0% PANI/PVP-EP immersed in 3.5% NaCl solution after 16 days at room temperature. Table 1 shows the corrosion parameters calculated from the Tafel region in Figure 7. The corrosion current densities (i_{corr}) of EP and PANI/PVP-EP calculated from Tafel regions are 101nA cm^{-2} (EP), 4.07 nA cm^{-2} (0.5% PANI/PVP-EP), 1.31 nA cm^{-2} (1% PANI/PVP-EP) and 4.26 nA cm^{-2} (2% PANI/PVP-EP), respectively. Obviously, the i_{corr} value of 1.0% PANI/PVP-EP was found to be less than that of 0.5% PANI/PVP-EP and 2.0% PANI/PVP-EP, which was only about one percent of EP. It is important to note that the PANI/PVP-EP exhibited more positive potential compared with EP coating (-0.701V). Hence, the PANI/PVP-EP showed better corrosion protection performance than neat EP.

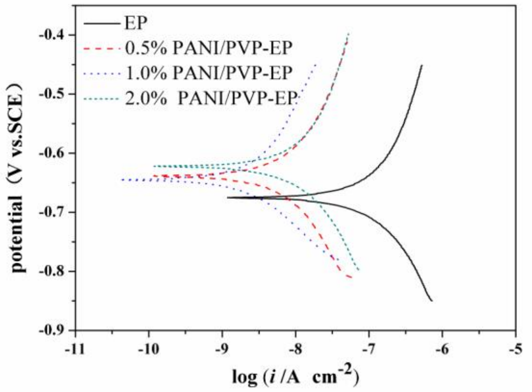

Figure 7. Polarization curves of PANI/PVP modified epoxy coatings immersed in 3.5% NaCl solution after 16 days.

Table 1. Corrosion parameters of PANI/PVP modified epoxy coatings immersed in 3.5% NaCl solution after 16 days.

	E_{corr} (V/vs.SCE)	i_{corr} (μA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})
EP	-0.701	101	368.2	-179.8
0.5% PANI/PVP-EP	-0.632	4.07	285.3	-255.4
1.0% PANI/PVP-EP	-0.654	1.31	222.2	-129.7
2.0% PANI/PVP-EP	-0.613	4.26	323.5	-299.4

EIS is one of the most intensively and nondestructive testing techniques for evaluating the corrosion protection performance of organic coatings [23, 24]. Figure 8 shows Nyquist and Bode plots of neat waterborne epoxy coating (EP), 0.5% PANI/PVP-EP, 1.0% PANI/PVP-EP and 2.0% PANI/PVP-EP immersed in 3.5% NaCl solution after different immersion times. The Bode plots showed one time constant at high frequency range in the initial stage of immersion (Stage I), and then another time constant at low frequency appeared due to the penetration of corrosive media during immersion process (Stage II) [25]. The neat EP displayed two time constants only after 1 day immersion, while 0.5% PANI/PVP-EP, 1.0% PANI/PVP-EP and 2.0% PANI/PVP-EP remains one time constant before 8, 16, and 16 days immersion, respectively. The impedance modulus at low frequency (such as $|Z|_{0.01Hz}$) is in inverse proportion to corrosion rate [26, 27]. The $|Z|_{0.01Hz}$ of 0.5% PANI/PVP-EP, 1.0% PANI/PVP-EP and 2.0% PANI/PVP-EP after 16-day immersion were 100 MΩ cm^2, 300 MΩ cm^2, and 138 MΩ cm^2, respectively, which were larger than that of neat EP (5.46 MΩ cm^2) after 10 days immersion. These results indicate that the addition of PANI/PVP nanoparticles significantly improved the corrosion protection of the epoxy coating, and the epoxy coating containing 1.0% PANI/PVP exhibited better anticorrosive performance.

Furthermore, equivalent circuits for stage I and II were employed to fit the EIS data of these four coatings (Figure 9) and the fitting corrosion parameters were listed in Table 2. In equivalent circuits, R_s is the solution resistance, and R_c and Q_c represent the coating resistance and capacitance, respectively. R_{ct} and Q_{dl} represent the charge-transfer resistance and double-layer capacitance, respectively [26]. After 8 days immersion, the R_c of 1.0% PANI/PVP-EP was 832.1 MΩ cm^2, which was much higher than that of neat EP (1.3 MΩ cm^2), 0.5% PANI/PVP-EP (0.57 MΩ cm^2) and 2.0% PANI/PVP-EP (79.7 MΩ cm^2) at the same immersion time. The R_{ct} of 1.0% PANI/PVP-EP and 2.0% PANI/PVP-EP did not emerge during 8 days immersion, probably due to that PANI/PVP nanoparticles improved passivation performance on carbon steel matrix [21]. These results further illustrate that 1.0% PANI/PVP-EP exhibited better corrosion protective effect based on carbon steel. According to some studies, the remarkably improved anticorrosion performance of PANI/PVP-EP could be attributed to the redox catalytic properties of PANI/PVP that induced the formation of oxide films and the inhibitory effect of doping anions [9, 21, 28, 29].

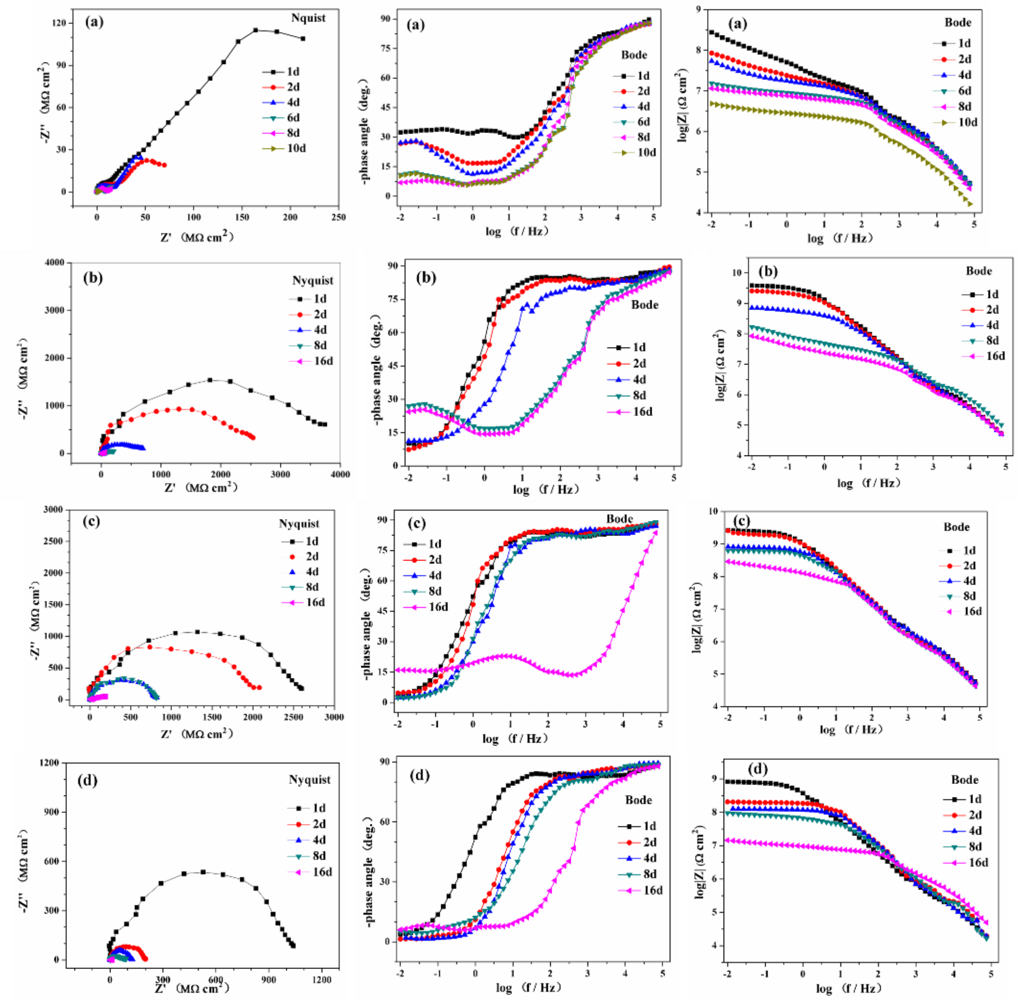

Figure 8 . Nyquist and Bode plots of epoxy coating systems containing different content of PANI/PVP immersed in 3.5% NaCl solution after different immersion times.(a):0%; (b):0.5%; (c):1.0% and (d) 2.0%.

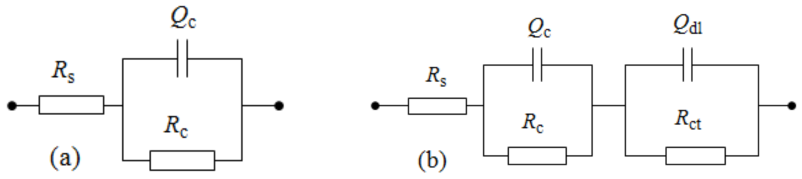

Figure 9. The equivalent circuit used to fit the EIS data.

Table 2. Electrochemical corrosion parameters fitted from the equivalent circuit.

PANI/PVP content	Immersion time days	R_s Ωcm ^{2}	Q_c nF cm^{-2}	n_1	R_c MΩ cm^2	Q_{dl} μF cm^{-2}	n_2	R_{ct} MΩ cm^2
0%	1	0.02	0.131	1.00	61.2	0.00848	0.51	515
	2	0.01	9.72	1.00	14.1	0.0747	0.53	97.9
	4	0.01	78.5	0.95	17.8	0.0859	0.57	68.4
	6	0.03	88.9	0.92	8.32	0.161	0.62	11.2

	8	0.01	374	0.94	1.13	0.562	0.54	3.57
	10	0.02	674	0.93	1.01	0.983	0.59	1.25
0.5%	1	0.03	0.181	0.70	4580			
	2	0.01	0.223	0.68	2888			
	4	0.07	0.435	0.61	710.3			
	8	0.07	4.87	0.62	0.571	0.387	0.49	271
	16	0.05	8.57	0.71	0.247	0.956	0.52	107
1%	1	0.01	0.189	0.70	3012			
	2	0.03	0.195	0.69	2456			
	4	0.08	0.247	0.67	881.2			
	8	0.01	0.397	0.66	832.1			
	16	0.01	4.95	1.00	0.216	0.364	0.46	235.6
2%	1	0.01	0.178	0.76	1211			
	2	0.03	0.214	0.74	204.3			
	4	0.07	0.248	0.72	128.6			
	8	0.08	4.31	0.69	79.7			
	16	0.03	7.97	0.92	1.35	67.1	0.65	4.42

4. CONCLUSIONS

Waterborne conductive PANI nanoparticles were prepared by dispersion polymerization using H_3PO_4 as dopant and PVP as stabilizer. The PANI/PVP nanoparticles showed regular spherical morphology with uniform diameters in the range of 60-80 nm. The PANI/PVP aqueous dispersion was easily incorporated into waterborne epoxy systems. The waterborne epoxy coating containing the PANI/PVP of 1.0 wt% exhibited better corrosion protective effect than pure epoxy coating, based on polarization curves and EIS measurements. The significantly enhanced anticorrosion performance could be attributed to the redox catalytic properties of PANI/PVP and the inhibitory effect of doping anions.

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