Electroactive poly(amic acid)-Cu²⁺ (EPAA-Cu) composites on the substrates have been prepared, whose electrochemical properties, including electroactivity, electrochromism and anticorrosion, reveal drastic enhancement after incorporation of Cu²⁺ ions.

Electrochemical performance of electroactive poly(amic acid)-Cu²⁺ composites

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ABSTRACT

Electroactive poly(amic acid)-Cu²⁺ (EPAA-Cu) composites on substrates were successfully prepared via nucleophilic polycondensation followed by the use of an immersing method. Analysis of the structure properties of EPAA-Cu composites was performed using scanning electron microscopy (SEM), X-ray photoelectron spectra (XPS) and Fourier-transform infrared spectra (FTIR). A significant current enhancement phenomenon of EPAA-Cu/ITO electrodes was found as evident from cyclic voltammetry (CV) measurements. In addition, Cu²⁺ ions were incorporated into

the composites and had a positive effect on their electrochromic behaviors decreasing their switching times. The anticorrosive performance of EPAA-Cu composites coatings on the carbon steel in 3.5 wt% NaCl solution were also investigated in detail using tafel plots analysis and electrochemical impedance spectroscopy. The anticorrosive ability of these coatings significantly enhanced through the incorporation of Cu^{2+} ions.

KEYWORDS: polyaniline; oligoaniline; electrochromic; anticorrosive

1. Introduction

As one of the most studied conducting polymers, polyaniline has received considerable investigation due to its simple synthesis, environmental stability, high conductivity, and numerous promising applications such as actuators, supercapacitors, sensors, antistatic coatings, electromagnetic shielding, and flexible electrodes [1-8]. Due to its poor processability, derived from large amount of intermolecular interaction and strong rigid backbone, polyaniline has few large-scale applications [9,10]. Therefore, design and synthesis of polyaniline derivatives with improved solubility and processability has gradually become a research hotspot. As alternative polymers for intractable polyaniline, oligoaniline-containing polymers (OCPs) feature enhanced solubility, processability and tunability, while retain much of polyaniline's functional capabilities. Consequently, several of OCPs including polyamides, polyimides, polyureas, poly(aryl ether)s, and polyolefins have been designed and prepared through various synthetic strategies [11-20], such as direct polymerization of

oligoaniline-functionalized monomers, and post-functionalization of polymers using oligoanilines. These synthesized OCPs with different topological structures, such as alternating, blocked, grafted, hyperbranched and networked have been applied to fabricate electrochromic devices, anticorrosive coatings, sensors, and tissue engineering materials [14-20].

To enhance the performance of the OCPs, some composites constituted from OCPs and nano-fillers have been prepared and reported [21-26]. Some versatile materials, such as graphene, multiwalled carbon nanotube, clay and silica nanoparticles, have also been incorporated into the OCPs matrix, which could significantly improve the mechanical properties, thermal properties, anticorrosive properties, sensing ability and even electronic **characteristics of OCPs**. For improvement of the practical applicability, more OCPs decorated with various fillers need to be further explored.

Therefore, in this work, we prepared EPAA-Cu composites on the substrates **using an immersing method**. Their electronic, **optical properties and anticorrosive properties were studied in detail to investigate their potential use as sensors, electrochromic windows, and anticorrosive coatings**.

2. Experimental

2.1. Materials

3,3',4,4'-Oxydiphthalic dianhydride (ODPA) were purchased from Shanghai Research Institute of Synthetic Resins. *N*-Phenyl-*p*-phenylenediamine was purchased from Aldrich. Ferric chloride, copper chloride, ammonium persulfate (APS), sodium

chloride, trimethylamine, hydrochloric acid (37%), ammonia water (25%), and hydrazine hydrate were obtained from Tianjin Chemical Factory. *N,N'*-Dimethylacetamide (DMAc), dichloromethane (DCM), tetrahydrofuran (THF), toluene, ethanol and acetone were purchased from commercial sources and used as received without further purification. Electroactive diamine (EDA) was used as the starting monomer for polycondensation, which was synthesized in our lab by a previously established synthetic route [27]. Optically transparent Indium-Tin Oxide (ITO) glass substrates were obtained from Reintech electronic technologies Co. Ltd (Beijing) and used as working electrode substrate in the electrochemical experiments. Q235 carbon steel (CS) were purchased from commercial source and used as working electrode substrate in anticorrosion measurements, whose composition (mass fraction, %) is: C 0.14-0.22, Mn 0.30-0.65, Si 0.3, S 0.05, P 0.045 and Fe bal.

2.2. General Methods

Fourier-transform infrared spectra (FTIR) measurements were recorded on a BRUKER VECTOR 22 Spectrometer in the range of 4000-400 cm^{-1} . Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-500 spectrometer for ^1H NMR in deuterated DMSO. The molecular weight information were determined with a gel permeation chromatography (GPC) instrument equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector using DMF as an eluent. The weight percentages of Cu in the polymer were obtained by inductively coupled plasma (ICP) atomic emission spectrometric analysis (PerkinElmer OPTIMA 3300DV). The X-ray photoelectron spectra (XPS) was performed on Thermo

ESCALAB 250 spectrometer. The morphologies of the polymer were observed by scanning electron microscopy (SEM, HITACHI, SU8020) coupled with Bruker energy dispersive X-ray spectrometer (EDX). Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer PYRIS 1 TGA in an air atmosphere. The electrochemical properties were investigated on a CHI 660A Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode cell, using an Ag/AgCl electrode as the reference electrode, a platinum wire electrode as the counter electrode. UV-vis spectra were taken on UV-3101 PC Spectrometer (SHIMADZU).

2.3. Synthesis of electroactive poly(amic acid)

A mixture of ODPA (3.100g, 10 mmol), EDA (6.842g, 10 mmol) and 50 mL DMAc was stirred at room temperature for 24 h under a nitrogen atmosphere. The synthetic route of EPAA is shown in Scheme 1. An EPAA DMAc solution was then obtained for the preparation of EPAA film.

^1H NMR ($\text{d}_6\text{-DMSO}$): δ =13.57-12.96 ppm (due to $-\text{COOH}$), δ =10.66-10.23 ppm (due to $-\text{CO-NH-}$), δ =7.46-7.73 ppm (due to $-\text{NH-}$), δ =7.51-6.46 ppm (due to Ar-H).

FTIR (KBr, cm^{-1}): 3436 ($\nu_{\text{N-H}}$), 1718 ($\nu_{\text{C=O}}$ of carboxylic acid), 1657 ($\nu_{\text{C=O}}$ of $-\text{CONH-}$ groups), 1576 ($\nu_{\text{C=C}}$ of quinoid rings), 1503 ($\nu_{\text{C=C}}$ of benzenoid rings), 1308 ($\nu_{\text{C-N}}$), 1156 ($\nu_{\text{N=Q=N}}$, where Q represents the quinoid rings), 833 ($\delta_{\text{C-H}}$). GPC data: Mw: 58200, PDI: 1.72.

2.4. Fabrication of the EPAA-Cu composites electrodes

ITO substrates were prepared with 3.5×0.5 cm dimension and ultrasonically washed with acetone, distilled water and ethanol for 3 min per solvent then air dried.

The obtained EPAA DMAc solution was diluted and filtered through 0.2- μ m syringe filter, and then spin-coated at 500 rpm for 10 s, then 1000 rpm for 30 s onto the ITO substrate for electroactivity and electrochromism measurements.

The CS substrates with the dimension of 2.0 $\times$ 1.0 $\times$ 0.1 cm were polished with emery papers and rinsed ultrasonically with acetone, distilled water and ethanol for 3 min per solvent, then dried in an oven. The filtered EPAA DMAc solution was cast on clean CS substrates for the anticorrosive measurements. The thickness of the EPAA coating on the CS substrates was controlled by varying EPAA DMAc solutions concentration and casting quantity.

The EPAA-Cu composites electrodes were fabricated by immersing the prepared EPAA modified electrodes into 0.05 mol/L CuCl₂ aqueous solution for different periods of times (10 s, 20 s, 30 s, 40 s, 50 s, and 180 s).

2.5. Anticorrosion performance

Polarization curve and electrochemical impedance spectroscopy were carried out to study the corrosive protection of EPAA and EPAA-Cu for the CS substrates in 3.5 wt% NaCl corrosive solution with CHI 660A Electrochemical Workstation. From polarization curves, some electrochemical corrosive parameters were calculated using the following equations. First, the polarization resistances (R_p) were calculated from the Tafel curves according to the Stearn-Geary equation [28-30]:

$$R_p = \frac{b_a b_c}{2.303(b_a + b_c)I_{corr}}$$

where I_{corr} is corrosion current, b_a and b_c are the anodic and cathodic Tafel slope ($\Delta E/\Delta \log I$), respectively. Corrosion rate (R_{corr} , in millimeter per year) was evaluated

using the following equation [31,32]:

$$R_{corr} = \frac{I_{corr}M}{DV} \times 3270$$

where I_{corr} is the corrosion current density (A/cm^2), M is the molecular weight of the metal subjected to corrosion (g/mol), V is the valence, 3270 is the constant and D is the density of the corroding metal (g/cm^3). The protection efficiency ($P_{EF\%}$) values were estimated using the following equation [33,34]:

$$P_{EF\%} = \frac{R_p^{-1}(\text{uncoated}) - R_p^{-1}(\text{coated})}{R_p^{-1}(\text{uncoated})} \times 100$$

3. Results and discussion

3.1. Characterization of EPAA-Cu composites

Scheme 1. Schematic representation of the preparation of EPAA and EPAA-Cu composites.

The EPAA-Cu composites on the ITO substrates were fabricated via nucleophilic polycondensation followed by immersion into a $CuCl_2$ bath, as shown in Scheme 1.

Due to the strong coordination between the Cu^{2+} ions and carboxylic acids, the Cu^{2+}

ions readily adsorbed onto the surface of EPAA coating during immersion. The amount of Cu^{2+} ions in the composite was adjusted by controlling the immersion time. In this study, the immersion times were set at 10, 20, 30, 40, 50, and 180 seconds, resulting in Cu-0.4 wt%, 1.0 wt%, 1.7 wt%, 2.4 wt%, 3.0 wt%, and 5.0 wt% EPAA-Cu composites (determined by ICP method). Here, the EPAA-Cu composites were defined as EPAA-Cu(0.4%), EPAA-Cu(1.0%), EPAA-Cu(1.7%), EPAA-Cu(2.4%), EPAA-Cu(3.0%), and EPAA-Cu(5.0%), respectively.

Figure 1. SEM images of EPAA (a) and EPAA-Cu(1.7%) (b) on the ITO substrate.

Inset of SEM image (b) shows Cu elemental mapping image from EDX spectrum for EPAA-Cu(1.7%) composite.

As shown in Fig. 1, the EPAA spin-coated on the ITO substrate formed a thin film with a 150 nm thickness, as determined by profilometer measurements. The EPAA coating appeared uniform and flat with few irregular particles. After immersing in the Cu^{2+} ions bath for 30 s, EDX mapping of copper shows a considerable amount of Cu^{2+} ions adsorbed on the surface of the EPAA coating (Inset of Fig. 1b). The uniform distribution of copper indicates successful fabrication of EPAA-Cu composites via an immersion method. Furthermore, no additional particles are seen from the formation of copper carboxylate complexes and the EPAA-Cu composite film has the same

thickness as the EPAA film.

Figure 2. XPS spectra of EPAA and EPAA-Cu(1.7%) composite: (a) survey, (b) Cu_{2p} and (c) N_{1s}.

A typical XPS survey scan reveals that the C, N and O signals are detected in the EPAA and EPAA-Cu coatings (Fig. 2a). The carbon, nitrogen, and oxygen 1s characteristic signals are observed and centered at 285 eV, 400 eV, and 534 eV, respectively. Typical copper 2p peaks are observed around 934 eV and 953 eV in the XPS spectra of EPAA-Cu composite, which illustrated that the surface of EPAA was modified with the addition of copper. In the Cu_{2p_{3/2}} core level spectra (Fig. 2b), a shoulder peak centered at 932.6 eV was observed due to the presence of Cu⁺. To this regard, the Cu_{2p} core level spectra is decomposed into two peaks centered at 934.4 eV and 932.6 eV, which correspond to Cu²⁺ and Cu⁺, respectively. The appearance of Cu⁺ is attributed to the redox reaction between oligoaniline segments and Cu²⁺ ions. Moreover, N_{1s} XPS spectra of EPAA and EPAA-Cu composite also exhibit expected variety as shown in Fig. 2c. The peak shape of N_{1s} XPS spectra of EPAA-Cu composite suggests the oxidation of amine groups. Consequently, the N_{1s} XPS core level spectrum of EPAA-Cu composite is decomposed into three peaks centered at 399.0 eV, 400.1 eV and 401.1 eV, which correspond to the quinonoid imine (=N-),

benzenoid amine (-NH-), and positively charged nitrogens (N⁺) from oxidized amine, respectively.

Figure 3. FTIR of EPAA and EPAA-Cu composites.

FTIR spectra of EPAA and EPAA-Cu showed the characteristic absorption bonds around 1718 cm⁻¹ and 1657 cm⁻¹ corresponding to C=O stretching vibration from the carboxylic acid and amide functional groups, as well as a band at 1308 cm⁻¹ due to the C-N stretching vibration. The absorptions around 1576 cm⁻¹ and 1503 cm⁻¹ are attributed to the stretching vibration of C=C in the quinoid and benzenoid rings, respectively. With the increase of copper in the composites, the intensity of C=C stretching vibration for quinoid rings increase obviously, again ascribed to the redox reaction between oligoaniline and Cu²⁺ ions.

3.2. Thermal properties

Figure 4. TGA thermograms of EPAA and EPAA-Cu composites.

The thermal stability of EPAA and EPAA-Cu composites was evaluated by TGA in an air atmosphere and are shown in Figure 4. The first weight loss begins at 160 °C due to dehydration from the imidization cyclization. The subsequent weight loss occurs in the temperature range 400–650 °C with a mass loss of 90%, which could be attributed to decomposition of the main chain. Due to the introduction of Cu^{2+} ions, the first weight loss of EPAA-Cu composites slightly decreases. In addition, the decomposition rate of the second weight loss for EPAA-Cu composites significantly increases. After running TGA measurements for EPAA-Cu composites there is some residual matter with constant weight due to the formation of copper oxide.

3.3. Electrochemical activity

Figure 5. (a) Representative CV curves of EPAA-Cu/ITO electrodes with different immersion times (0, 10, 20, 30, 40, 50, and 180 s) at the potential scan rates of 100 mV/s. (b) CV of EPAA-Cu(1.7%)/ITO electrode in 0.5 M H₂SO₄ at different potential scan rates: 10-100 mV/s. Inset shows the relationships between the oxidation and reduction current vs. potential scan rate.

The electrochemical activities of EPAA-Cu composites were studied by cyclic voltammetry (CV) using a traditional three-electrode system in 0.5 M H₂SO₄ solution. The EPAA-Cu/ITO was used as the working electrode in the measurement system. Before immersion into a CuCl₂ bath, the CV curve of EPAA exhibits two pairs of redox peaks at 0.35 V/0.17 V, and 0.50 V/0.31 V (Fig. 5a), which are assigned to the transition of leucoemeraldine base (LEB)/emeraldine base (EB), and EB/peryraniline base (PNB), respectively. After the insertion of Cu²⁺ ions, the electrochemical activity changed dramatically. Some positive shift are observed for the oxidative peaks, while the reductive peaks exhibit little negative shift. A current enhancement phenomenon was also found for these redox peaks after the electrode was immersed into the CuCl₂ bath. When the immersion time increase to 30 s, the peak current at 0.54 V increases to 1.6 times its original value, which is also the maximum current value observed from the incorporation of Cu²⁺ ions. This current enhancement phenomenon indicates that the conductivity of the electrode material was enhanced through the incorporation of Cu²⁺ ions. When using extended immersion time, the EPAA-Cu/ITO electrode experiences reduced current enhancement, the cause of these results are still being explored in our lab.

Furthermore, a linear dependence of the peak currents, as a function of scan rates in the region of 10-100 mV/s, confirmed a surface controlled process of EPAA-Cu(1.7%) in the electrochemical measurement (Fig. 5b).

3.4. Optical properties

Figure 6. UV-vis spectra of EPAA-Cu/ITO with different content of Cu^{2+} ions. The inset shows photographs of EPAA-Cu/ITO with different content of Cu^{2+} ions.

After spin-coated on the ITO substrate, the EPAA thin film with the thickness of 150 nm would be to some extent oxidized. Due to their original carboxylic acid groups, the EPAA films present a partially doped state. As shown in Fig. 6, there are three absorption peaks at about 295 nm, 435 nm and 550-800 nm, which are ascribed to π - π^* transition in the benzoid ring, polaron- π^* transition and π -polaron transition. This represents the formation of conducting state of EPAA. After immersion into Cu^{2+} ions bath, the intensity of the π -polaron transition increases indicating that the conductivity is enhanced by the introduction of Cu^{2+} ions. The photographs of EPAA-Cu/ITO record the process as a gradual darkening.

3.5. Electrochromic performance

Figure 7. The spectral changes of (a) EPAA/ITO electrode and (b)

EPAA-Cu(1.7%)/ITO electrode in 0.5 mol/L H₂SO₄ at different potentials, and the

inset shows photographs of electrochromic electrode at different potentials; (c)

transmittance changes monitored at 700 nm of the two electrodes when the applied

potential was switched between 0 V and 0.8 V with a residence time of 30 s.

In view of the unique photophysical properties as well as reversible electrochemical activity, the EPAA-Cu composites show potential to be used as electrochromic materials. Consequently, the electrochromic performance of EPAA and EPAA-Cu composites were comparatively investigated through spectroelectrochemical experiments and spectrochronoamperometry measurements. The EPAA/ITO and EPAA-Cu/ITO electrodes were prepared as the working electrodes. A 0.5 M H₂SO₄ aqueous solution was used as the electrolyte. In the spectroelectrochemical experiments, the electrochromic films were measured with applied potentials of -0.2, 0, 0.2, 0.4, 0.6, 0.8 and 1.0 V (vs Ag/AgCl), in conjunction with the acquisition of UV-vis spectral data. As shown in Fig. 7, obvious changes in UV-vis transmittance spectra are observed with different applied potentials. However, both the electrochromic electrodes exhibit very similar optical change regulation. The EPAA

film revealed a moderate optical contrast value ($\% \Delta T$) of 43% at 700 nm between its colored and bleached states. After the incorporation of Cu^{2+} ions, the optical contrast value decrease to 38% due to the intrinsic absorbance of Cu^{2+} ions at 700 nm. Both electrochromic films show the same color change regulation, from gray (at -0.2 V), to green (at 0.4 V), and finally to black blue (at 1.0 V).

The spectrochronoamperometry measurements of EPAA and EPAA-Cu composite electrochromic electrodes were also been carried out to monitor the changes in the optical contrast at 700 nm during repeated potential stepping between 0 V and 0.8 V with a residence time of 30 s. This could present some important electrochromic parameters, such as switching time and coloration efficiency. The switching time is the time required to bring electrochromic material to its reduced state from its oxidized state or vice versa, which was defined here as the time required for reaching 90% of the full change in coloring/bleaching process. The coloration efficiency (CE) was determined by monitoring the amount of ejected charge as a function of the change in optical density of the electrochromic film, which is used to measures the power requirements of an electrochromic material. In our measurement, the EPAA film revealed a moderate CE about $59 \text{ cm}^2/\text{C}$ (at 700 nm) with a fast switching time of 5.3 s at 0.8 V for the coloring process and 3.2 s at 0 V for bleaching. As for the EPAA-Cu composite material, the CE was found decreasing to $51 \text{ cm}^2/\text{C}$. However, the switching times have been observed greatly enhanced to 1.9 s at 0.8 V and 1.0 s at 0 V, which could be attributed to the enhanced conductivity of the modified electrode materials. All of the obtained evaluation parameters for electrochromic behavior

demonstrated that EPAA-Cu composites are good candidates for use as electrochromic materials.

3.6. Anticorrosion behavior

Figure 8. (a) Tafel plots for EPAA/CS corrosive electrodes with various thicknesses (5, 10, 20, 40, and 60 μm); (b) Tafel plots for EPAA/CS corrosive electrodes (5 μm) with different immersion time (0, 10, 20, 30, 40 and 50 s).

In consideration of their reversible electrochemical activity and good film-forming ability, the obtained EPAA and EPAA-Cu composites were expected to be potential candidates for corrosive protection material. Firstly, polarization technique was carried out to study the corrosive protection of EPAA and EPAA-Cu for CS in 3.5 wt% NaCl solution, where the large cathodic and anodic polarizations provide curves for the respective corrosion process. In the conventional three-electrode system, platinum wire electrode, a saturated calomel electrode, and a modified CS electrode were used as counter electrode, reference electrode, and working electrode, respectively. The thickness of EPAA coatings were controlled at 5, 10, 20, 40, and 60 μm (measured by spiral micrometer) using the casting method. As expected, classic Tafel curves of

EPAA/CS with different thickness were presented in Fig. 8a. Tafel extrapolation method was applied on the Tafel curves to calculate corrosion potential (E_{corr}) and corrosion current density (I_{corr}). After coated with EPAA (5, 10, 20, 40, and 60 μm), the E_{corr} of the EPAA/CS electrodes underwent a significantly positively shift from -0.787 V to -0.457 V, -0.063 V, 1.05 V, 1.74 V, and 2.28 V. The I_{corr} decrease drastically from 21.84 $\mu\text{A}/\text{cm}^2$ to 1.477 $\mu\text{A}/\text{cm}^2$, 0.1629 $\mu\text{A}/\text{cm}^2$, 0.02267 $\mu\text{A}/\text{cm}^2$, 0.002660 $\mu\text{A}/\text{cm}^2$ and 0.001623 $\mu\text{A}/\text{cm}^2$. According to the relevant equations, more electrochemical corrosion parameters, such as R_p , R_{corr} and P_{EF} , have been calculated and are presented in Table 1. With an increase of thickness, the R_{corr} of specimens decrease drastically from 0.170 mm/year to 1.26×10^{-5} mm/year. The corresponding P_{EF} is calculated as high as 99.99%, when the thickness of EPAA coating increase to 60 μm , which confirms the availability of corrosive protection through the incrassation of EPAA coatings. In conclusion, these results indicated that EPAA could be good candidates for use as corrosive protection material for CS substrates.

Table 1. Electrochemical corrosion parameters of the EPAA/CS samples with various thicknesses (0, 5, 10, 20, 40, and 60 μm) in 3.5 wt% NaCl solution.

Sample	E _{corr} (V)	I _{corr} ($\mu\text{A}/\text{cm}^2$)	R _p ($\text{K}\Omega\text{ cm}^2$)	R _{corr} (mm/year)	P _{ef} %
blank	-0.787	21.84	0.05000	0.1700	--
5 μm	-0.457	1.477	0.8710	1.150×10^{-2}	94.25
10 μm	-0.0630	0.1629	7.910	1.271×10^{-3}	99.36
20 μm	1.05	0.02267	74.94	1.760×10^{-4}	99.93
40 μm	1.74	0.002660	342.3	2.070×10^{-5}	99.98
60 μm	2.28	0.001623	1075	1.263×10^{-5}	99.99

Table 2. Electrochemical corrosion parameters of the EPAA-Cu/CS samples with different immersion time (0, 10, 20, 30, 40, and 50 s) in 3.5 wt% NaCl solution. The thickness of EPAA coating is about 5 μm .

Sample	E _{corr} (V)	I _{corr} ($\mu\text{A}/\text{cm}^2$)	R _p ($\text{K}\Omega\text{ cm}^2$)	R _{corr} (mm/year)	P _{ef} %
blank	-0.787	21.84	0.05000	0.1700	--
0 s	-0.457	1.477	0.8710	1.150×10^{-2}	94.25
10 s	-0.439	0.7406	1.821	5.761×10^{-3}	97.26
20 s	-0.322	0.6408	2.151	4.981×10^{-3}	97.68
30 s	-0.271	0.5617	2.480	4.370×10^{-3}	98.06
40 s	-0.248	1.050	1.322	8.173×10^{-3}	96.26
50 s	-0.223	1.128	1.213	8.772×10^{-3}	95.87

The EPAA-Cu/CS corrosive electrodes were also prepared by immersing into Cu^{2+} bath. The immersion times were set at 10, 20, 30, 40, and 50 s, which would result in Cu-0.0014 wt%, 0.003 wt%, 0.005 wt%, 0.007 wt%, and 0.009 wt%, composites (determined by ICP method). The corrosive protection properties of EPAA-Cu composites for the CS substrate were then investigated by polarization technique. From the obtained Tafel curves (in Fig. 8b), all the detailed electrochemical corrosion

parameters were calculated through Tafel extrapolation method and relevant equations, and are presented in the Table 2. With an increase of the immersion time, a significantly positive shift of E_{corr} for EPAA-Cu composites was found, enhancing from -0.457 V (0 s) to -0.223 V (50 s). However, the corresponding I_{corr} , R_p , R_{corr} , and P_{EF} reveal nonlinear characteristic. When the EPAA/CS electrode was immersed into the Cu^{2+} bath for 30 s, all of the corrosion parameters achieve optimum properties and the P_{EF} of EPAA-Cu composites to CS substrate show high values up to 98.06%.

Figure 9. (a) EIS for EPAA/CS corrosive electrodes with various thicknesses (5, 10, 20, 40, and 60 μm); (b) EIS for EPAA-Cu/CS corrosive electrodes (5 μm) with different immersion time (0, 10, 20, 30, 40, and 50 s).

Electrochemical impedance spectroscopy (EIS) measurements were also performed on EPAA and EPAA-Cu coatings to study the corrosion protection behavior for CS substrates. All the Nyquist plots of the samples were fitted by Randles type equivalent circuit model, which are usually used to simulate the experimental data at the initiate state. The film resistance (R_f) of all the samples were determined by the intersection of the low-frequency end of the semicircle arc with the real axis. Fig. 9a represents

Nyquist plots of EPAA/CS coatings with different thickness in the 3.5 wt% NaCl solution. With an increase of coating thickness, the R_f of EPAA/CS coatings increases from 248 to 25660, 78226, 657822, 1641091, 2041629 Ω . After EPAA/CS coatings (thickness of 5 μm) immersing into Cu^{2+} bath, the R_f of EPAA-Cu/CS composite coatings increases to 25660, 27302, 32766, 33912, 23853, 22884 Ω with the immersion time increasing from 0 to 10 s, 20 s, 30 s, 40 s, and 50 s. It's worth noting that the EPAA-Cu composite coating with 30 s immersion shows the maximum value of R_f , which was the same requirement as that for optimal electrochemical activity. These results demonstrate that a tiny amount of Cu^{2+} ions in the anticorrosive coatings would improve the corrosive protection greatly. The EPAA-Cu composite coatings have been proved to be effective anticorrosive material for the CS substrate.

4. Conclusion

EPAA-Cu composites, prepared via nucleophilic polycondensation followed by an immersing method, exhibited interesting spectroscopic properties and an improved electrochemical performance. After incorporating Cu^{2+} ions, the modified electrodes revealed a significant current enhancement phenomenon, which effectively reduced the switching times for their electrochromic behaviors. In addition, EPAA-Cu coatings on carbon steel provided effective corrosive protection in a 3.5 wt% NaCl solution, again due to the incorporation of Cu^{2+} ions on the surface of the coatings. The investigation of EPAA-Cu composites not only paves the way of their practical application, but also inspired us to explore the new characteristic for similar polymer composites.

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Figure Captions

Scheme 1. Schematic representation of the preparation of EPAA and EPAA-Cu composites.

Figure 1. SEM images of EPAA (a) and EPAA-Cu(1.7%) (b) on the ITO substrate. Inset of SEM image (b) shows Cu elemental mapping image from EDX spectrum for EPAA-Cu(1.7%) composite.

Figure 2. XPS spectra of EPAA and EPAA-Cu(1.7%) composite: (a) survey, (b) Cu_{2p} and (c) N_{1s}.

Figure 3. FTIR of EPAA and EPAA-Cu composites.

Figure 4. TGA thermograms of EPAA and EPAA-Cu composites.

Figure 5. (a) Representative CV curves of EPAA-Cu/ITO electrodes with different immersion times (0, 10, 20, 30, 40, 50, and 180 s) at the potential scan rates of 100 mV/s. (b) CV of EPAA-Cu(1.7%)/ITO electrode in 0.5 M H₂SO₄ at different potential scan rates: 10-100 mV/s. Inset shows the relationships between the oxidation and reduction current vs. potential scan rate.

Figure 6. UV-vis spectra of EPAA-Cu/ITO with different content of Cu²⁺ ions. The inset shows photographs of EPAA-Cu/ITO with different content of Cu²⁺ ions.

Figure 7. The spectral changes of (a) EPAA/ITO electrode and (b) EPAA-Cu(1.7%)/ITO electrode in 0.5 mol/L H₂SO₄ at different potentials, and the inset shows photographs of electrochromic electrode at different potentials; (c) transmittance changes monitored at 700 nm of the two electrodes when the applied potential was switched between 0 V and 0.8 V with a residence time of 30 s.

Figure 8. (a) Tafel plots for EPAA/CS corrosive electrodes with various thicknesses (5, 10, 20, 40, and 60 μm); (b) Tafel plots for EPAA/CS corrosive electrodes (5 μm) with different immersion time (0, 10, 20, 30, 40, and 50 s).

Figure 9. (a) EIS for EPAA/CS corrosive electrodes with various thicknesses (5, 10, 20, 40, and 60 μm); (b) EIS for EPAA-Cu/CS corrosive electrodes (5 μm) with different immersion time (0, 10, 20, 30, 40, and 50 s).