Graphene Oxide/Polyaniline Nanocomposites Used in Anticorrosive Coatings for Environmental Protection

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Abstract: In recent years, metal corrosion causes serious threats to the economy of the world and the living environment. Hence, it is very important to seek non-toxic and environmentally friendly materials with metal anti-corrosion properties for the sustainable development of society. The barrier properties of graphene oxide (GO) and the special electrochemical property of polyaniline (PANI) can significantly improve the corrosion resistance of metals. Herein, we developed an in-situ polymerization method to prepare graphene oxide/polyaniline (GO/PANI) nanocomposites with unique anti-corrosion properties. The obtained GO/PANI nanocomposites were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermalgravimetric analysis, UV–vis spectroscopy and scanning electron microscopy. The as-prepared composite materials were uniformly dispersed in epoxy resin to prepare anticorrosive coatings and coated on the surface of steel. The anti-corrosion performance of the coatings was measured by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization technique. The EIS results showed that the total impedance of epoxy/GO/PANI coatings is greater than epoxy/PANI coatings, and the impedance module value can reach 8.67 × 10⁸ Ω·cm². In general, it is concluded that the anti-corrosion performance of GO/PANI coating is significantly higher than PANI coating and pure GO coating.

Keywords: polyaniline; graphene oxide; epoxy resin; corrosion

1. Introduction

Metal corrosion is a phenomenon that metallic material is destroyed by the surrounding medium. Nowadays, metal corrosion has been a common problem faced by all countries in the world, due to that it significantly reduces the mechanical properties of metal materials and the service life of metal equipment. Therefore, metal corrosion must be prevented and controlled. Among the numerous anti-corrosion methods, anticorrosive coatings are a kind of simplest, most extensive, effective and economical method [1,2]. Corrosion inhibitors containing heavy metals such as Pb, Cr, Zn, etc. are often added to traditional anticorrosive coatings. The residue of these heavy metals will cause great harm to human health and the ecological environment. Therefore, it is of great significance for the sustainable development of society to seek non-toxic and bio-environmentally friendly coatings with metal anti-corrosion properties.

In recent years, the addition of conductive polymers to organic coatings to inhibit metal corrosion has become a research hotspot. Among the conducting polymers, polyaniline (PANI) is most promising due to its ease of synthesis, non-toxic, low cost, excellent chemical and environmental stability, as well as reversible redox properties [3–5]. PANI has been widely used in the fields of batteries, catalysts, sensors, light-emitting diodes, electrochromic and anti-corrosion coatings [6–8], etc. Since DeBerry [9] discovered
that PANI deposited on the metal surface can effectively prevent metal corrosion, the research of PANI in the field of coating corrosion has become a hot spot. A large number of scholars have done sufficient research and analysis on the anticorrosion mechanism of PANI. Currently, there are three widely recognized anticorrosion mechanisms: shielding, metal passivation and anode protection [10–13]. Due to the unique redox reversibility, electrical conductivity and excellent environmental stability, PANI has been used as a protective coating for various types of metals, such as stainless steel [14], iron [15,16], mild steel [17], copper [18] and so on [19,20]. However, PANI is difficult to process and easy to agglomerate [21], which will affect its performance in coatings. Therefore, surface modification of PANI to improve its dispersibility is one of the effective methods to improve its corrosion resistance.

Graphene is a hexagonal honeycomb two-dimensional crystal material composed of sp2 carbon [22,23], which has been widely used in various fields recently due to its high thermal and electrical conductivity, sheet structure, non-toxic and barrier property [24,25]. Graphene oxide (GO) is an important derivative of graphene [26], which has a similar structure and performance as graphene. There are rich oxygen functional groups on the surface of GO (e.g., carboxyl groups, epoxy groups, hydroxyl groups, etc.), which make it easier to compound with other materials [27]. GO also has good heat resistance, chemical solvent resistance and excellent barrier properties, these properties provide a good theoretical basis for the research of GO in anticorrosive coatings. Chang et al. [28] firstly proposed the application of polyaniline/graphene composites in corrosion protection of steel, found that compared with pure polyaniline and polyaniline/clay composites, the polyaniline/graphene composites showed more excellent barrier properties to O2 and H2O. Yu et al. [29] prepared well-dispersed polystyrene/modified GO composite materials through in-situ microemulsion polymerization and used them for corrosion protection. The results showed that after adding 2% modified GO to the polystyrene polymer matrix, the anti-corrosion efficiency of the composite material increased from 37.90% to 99.53%. Krishnamoorthy et al. [30] developed a multifunctional GO nano-coating by cross-linking GO and alkyd resin lipid chains, which showed anti-corrosion and antibacterial effects. The prepared GO nano paint exhibited excellent anti-corrosion performance and antibacterial properties. GO and PANI are both non-toxic and anticorrosive materials, so it can be considered as composite materials to improve their performance in coatings.

In recent years, the application of GO/PANI nanocomposites in corrosion protection has been reported. Mooss et al. [31] successfully prepared a series of polyaniline–graphene oxide (PANI–GO) nanocomposites by altering the GO content, and the obtained PANI–GO nanocomposites displayed excellent dispersive and crystalline performance. The prepared conductive anticorrosive coating has long-term corrosion resistance, which shows good anticorrosive performance after being immersed in 3.5 wt.% NaCl solution for 96 h. Lin et al. [32] prepared a poly(styrenesulfonate)-polyaniline/reduced GO composite and added it into epoxy resin as anticorrosive filler to prepare the epoxy coating, and the mechanical and anticorrosive properties was studied. The results showed that the ultimate tensile strength and tensile toughness of epoxy composites increased by 39% and 127% respectively, and the lower corrosion rate showed that the anti-corrosion efficiency was greatly improved. Ramezanzadeh et al. [33] prepared graphene oxide-polyaniline (GO–PANI) composites with high crystallinity and conductivity and studied the effects of GO and GO–PANI on corrosion resistance and mechanism of ZRC. The addition of GO–PANI filler not only enhances the barrier performance of ZRC, but also extends the cathodic protection time and significantly improves the electrical contact between the zinc particles and the steel substrate. Both GO and PANI have an anticorrosive effect on the metal matrix, but the anticorrosive mechanism of the two is not the same. Except as small particles filled into the coating pores and defects, PANI anticorrosive coatings mainly rely on the oxidation-reduction reaction of PANI (the conversion between oxidation state, intermediate state, and reduced state) to improve the anticorrosive performance of the coating. While the GO anti-corrosion coatings rely on physical shielding and electrochemical anti-corrosion of the two-dimensional graphene sheets in the coatings. Therefore, the dispersion and anticorrosive performance of the composite materials obtained
by compounding GO and PANI is significantly improved. The non-toxic and environmentally friendly GO/PANI coatings are multifunctional coatings for anti-corrosion.

In the present investigation, the GO/PANI nanocomposites were prepared by in-situ polymerization. By controlling the content of GO, different GO/PANI composites were prepared and dispersed uniformly in epoxy resin to prepare anticorrosive coatings. The resulting samples were characterized by Fourier transform infrared (FT-IR), UV–vis spectroscopy (UV–vis), and X-ray diffraction (XRD). The thermal properties of the materials were studied by thermogravimetric analysis (TGA) analysis, the anticorrosive performance of epoxy coatings was investigated using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. In this study, the PANI-GO (4 wt.%) coating shows the best anti-corrosion performance, which is much better than the PANI and pure epoxy coating.

2. Materials and Methods

2.1. Materials

Graphene powder was purchased from Qingdao Risheng Co., Ltd. (Qingdao, China), sulfuric acid (H_2SO_4, 98%), sodium nitrate (NaNO_3), concentrated hydrochloric acid (HCl), sodium chloride (NaCl), ethanol (C_2H_5OH 99.5%) and potassium permanganate (KMnO_4) were obtained from Aladdin Co. (Shanghai, China). Aniline monomer (An), ammonium persulfate (APS) and hydrogen peroxide (H_2O_2, 35%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents were of analytical grade and used without further processing. Epoxy resin (E-44) and harder (polyamide 650) were purchased from Jiangsu Zhenjiang Danbao Resin Co., Ltd. (Zhenjiang, China). Steel plate obtained from Dongguan Chuicheng Metal Material Co., Ltd. (Dongguan, China) was used as the substrate. Distilled water was produced by the laboratory.

2.2. Preparation of GO

We used a modified hummers method to prepare GO. Firstly, mixed 5 g of graphite powder and 2.5 g of NaNO_3 in a 1000 mL round bottom flask with 115 mL of concentrated H_2SO_4 in an ice bath for about 15 min. Then, we added 15 g of KMnO_4 in batches within 1 h, and continuously stirred for 2 h. In the next step, raised the temperature to 35–40 °C, and continuously stirred for 4 h. After that, we added 150 mL of distilled water to a flask and set the temperature at 98 °C with continuous stirring for 30 min. We terminated the reaction after adding a large number of distilled water. Finally, we slowly added H_2O_2 solution until the reaction no longer generated bubbles. The reactant was centrifuged and washed with dilute hydrochloric acid until the sulfate ions were completely removed, and then washed with distilled water to neutrality to obtain 0.02 wt.% GO suspension. The specific preparation process is shown in Figure 1.

Figure 1. Preparation of graphene oxide (GO)/polyaniline (PANI).
2.3. Preparation of Graphene Oxide/Polyaniline (GO/PANI) Nanocomposites

The reaction was carried out at −5~0 °C under continuous stirring. Different content of GO (0, 1, 2, 3, 4, and 5 wt.%) was added into 25 mL deionized water and ultrasonicated for 30 min to get a uniform solution. Then, aniline (2.33 g) was added to the GO suspension. The APS (2.00 g) was dissolved in 40 mL of 1 M HCl and stirred up for 10 min. Finally, the APS solution was slowly added to the flask dropwise. Under the ice bath and magnetic agitation condition, the reaction lasted for 6 h. The GO/PANI was repeatedly washed with distilled water and ethanol, and then dried at 60 °C in a vacuum for 24 h.

2.4. Preparation of Coatings

GO, PANI and GO/PANI nanocomposites were taken into 2 mL ethanol respectively, and ultrasonically dispersed for 20 min. Afterwards, 3 g of epoxy resin (E-44) was added to the above solution and dispersed at high speed for 30 min. We added 2 g of harder (polyamide 650) to this mixture, and then put the sample in a centrifuge tube, through which the bubbles of the coating are removed. Prior to coating, the steel plate (10 × 10 × 2 mm³) was polished with emery papers (grade 500, 1000, and 2000), degreased with ethanol, and dried. The above mixture was uniformly coated on the surface of the steel plate with a wire rod coater to control the coating thickness to 60 µm. Finally, coatings were cured at room temperature for 24 h, then put in an oven at 60 °C to dry for 24 h. Different coatings were prepared by the same method, which are denoted as pure epoxy, GO, PANI, PANI–GO(1 wt.%)(PG1), PANI–GO(2 wt.%)(PG2), PANI–GO(3 wt.%)(PG3), PANI–GO(4 wt.%)(PG4) and PANI–GO(5 wt.%)(PG5), respectively.

2.5. Characterization

The surface morphology of the materials was characterized by a scanning electron microscope (TecnaiG220, FEI, Hillsboro, OR, USA). Fourier Transform Infrared spectroscopy (Avatar 360 Nicolet, Thermo Fisher Scientific, Waltham, MA, USA) was employed to investigate the surface functional groups of materials. X-ray powder diffraction tests were performed on Cu-Kα radiation (DY5261/Xpert3, PANalytical B.V., Malvern Panalytical, Malvern, UK), the scan range is from 10° to 90° and the scanning speed is 0.2°/s. UV–vis spectroscopy was performed by UV–vis spectrophotometer (TU-1900, Beijing Puxi General Instrument Co., Ltd., Beijing, China) in the wavelength region from 200 to 800 nm. Thermogravimetric analysis was employed with an automatic sampling synchronous thermal analyzer instrument (STA449F5, Selb, Germany), with heating from room temperature to 900 °C at a rate of 10 °C/min under an N₂ atmosphere. For the corrosion studies, a conventional three-electrode cell system was assembled by the coated steel panel as working electrode, platinum as a counter electrode and a saturated calomel electrode (SCE) as a reference in an electrolyte of 3.5 wt.% NaCl solution. Electrochemical impedance spectroscopy (EIS) measurements and potentiodynamic polarization curves were done by the CHI-650E electrochemical workstation (Shanghai CH Instrument Company, Shanghai, China).

3. Results and Discussion

3.1. SEM Analysis

Figure 2 shows the scanning electron microscopy (SEM) images of GO, PANI and GO/PANI composites. As shown in Figure 2a, the pure GO has a flaky structure with the surface is smooth and pleated. The SEM image of the pure PANI presents short-rod morphology with partially agglomerated in some sections. It can be seen from Figure 2c that the flaky structure of GO is still retained, while PANI accumulates on both the surface of GO and the intercalation with the agglomeration phenomenon is significantly reduced and the morphology of PANI has changed. It shows that the GO/PANI composite was successfully synthesized, and the dispersion of PANI was enhanced.
3.2. XRD Analysis

The crystal structures of the different samples were studied by powder X-ray diffraction (XRD) measurements. Figure 3 shows the XRD patterns of GO, PANI, and GO/PANI composites. The XRD pattern of GO revealed an intense and sharp reflection peak at $2\theta = 8.8^\circ$ (001), corresponding to a spacing of 1.0 nm. This interlaminar distance is due to the presence of oxygen-containing groups (such as carboxyl, epoxy, hydroxyl) and water absorption in the GO structure [34]. In the case of PANI, the characteristic peaks at 8.4°, 15.1°, 20.1°, 25.3°, 26.8° and 29.2°, correspond to (001), (011), (020), (200), (121), and (022) diffraction planes of emeraldine salt form PANI, respectively [35,36]. The XRD patterns of synthesized GO/PANI nanocomposites are the same as that of PANI, which indicates that the molecular chain structure of PANI was not destroyed. No obvious peak of GO was observed in the XRD pattern of GO/PANI, indicating that the GO has almost no agglomeration, but fully reacted with the polymerization reaction substrate to synthesize the GO/PANI nanocomposite [37].

![SEM images of (a) GO, (b) PANI and (c) GO/PANI nanocomposites.](image1)

Figure 2. SEM images of (a) GO, (b) PANI and (c) GO/PANI nanocomposites.

3.3. FT-IR Analysis

Figure 4 shows the FT-IR spectra of the GO, PANI and PANI/GO nanocomposites in the region of 3900–500 cm$^{-1}$, respectively. In the FT-IR spectra of the GO, there is a wide peak near at 3420 cm$^{-1}$, which is caused by the tensile vibration of the O–H bond group in GO [15]. The peaks at 1740 and 1620 cm$^{-1}$ are attributed to the C–O, C=O in COOH, and peaks at 1210 and 1050 cm$^{-1}$ are caused by the vibration of –OH, and C–O–C, respectively [38,39]. For the PANI, the peaks at 1580 and 1480 cm$^{-1}$ correspond to the characteristic C=C stretching mode of the quinoid and benzenoid rings, respectively [40]. Peaks at 1130 and 804 cm$^{-1}$ are assigned to in-plane and out-of-plane bending of C–H [41]. These absorption bands are significantly decreased in the FTIR spectra of the GO/PANI, indicating that most of the functional groups had been substantially removed by chemical reduction. The mainly characteristic peaks of the GO/PANI composite shows are similar to the peaks of PANI, and it shows the characteristic peak of O–H of GO at 3430 cm$^{-1}$. From the spectrum of the GO/PANI nanocomposite, all the characteristic peaks of PANI and GO can be found, indicating the nanocomposite successfully prepared.

![X-ray diffraction (XRD) patterns of GO, PANI and GO/PANI nanocomposites.](image2)

Figure 3. X-ray diffraction (XRD) patterns of GO, PANI and GO/PANI nanocomposites.
was studied by TGA analysis. The initial mass loss of all materials approximately occurred at 120 °C.

The first step of weight loss is observed with 12% weight loss at ~120 °C due to the evaporation of moisture from the samples. For the GO, the first weight loss of ~15% at 300–600 °C can be attributed to the removal of more stable oxygen-containing functional groups (hydroxyl, carboxylic acid and epoxide) in GO, and these functional groups are highly consistent with the absorption peaks of GO in previous reports [31]. The two characteristic peaks of PANI appeared at 359 and 691 nm, which was attributed to the π–π* transition of an aromatic C–C bond and a quinonoid C–C bond, respectively [24]. The spectrum for GO/PANI composites is similar to that for the PANI sample, except a new absorption band at 235 nm, which corresponds to the presence of GO. This result clearly shows the successful in-situ compounding of GO in the composites.

Figure 4. Fourier transform infrared (FT-IR) images of GO, PANI and GO/PANI nanocomposites.

3.4. UV–Vis Analysis

Figure 5 illustrates the UV–vis absorption spectra of GO, PANI and GO/PANI nanocomposites dispersion in ethanol solution. The UV–vis spectrum of neat GO includes a sharp peak at 227 nm is attributed to the π–π* transition, and there is a shoulder peak at 295 nm is related to the n–π* transition, showing that there are some oxygen-containing functional groups (hydroxyl, carboxylic acid and epoxide) in GO, and these functional groups are highly consistent with the absorption peaks of GO in previous reports [42,43]. The two characteristic peaks of PANI appeared at 359 and 691 nm, which was attributed to the π–π* transition of an aromatic C–C bond and a quinonoid C–C bond, respectively [24]. The spectrum for GO/PANI composites is similar to that for the PANI sample, except a new absorption band at 235 nm, which corresponds to the presence of GO. This result clearly shows the successful in-situ compounding of GO in the composites.

Figure 5. UV–vis spectra of (a) PANI, GO/PANI and (b) GO.

3.5. TGA Analysis

As shown in Figure 6, the thermal behavior of GO, PANI and GO/PANI nanocomposites samples was studied by TGA analysis. The initial mass loss of all materials approximately occurred at 120 °C due to the evaporation of moisture from the samples. For the GO, the first weight loss of ~15% at ~120 °C is due to the loss of the evaporation of physically adsorbed moisture in the samples. The weight loss in the next stage between 120 and 300 °C (about 45%) is due to the decomposition of carbon oxidation and oxygen-containing functional groups [42,43]. A lighter weight loss of 14% from 300 to 900 °C can be attributed to the removal of more stable oxygen-containing functional groups and the decomposition of GO ring chains. For the PANI, the main weight loss was divided into three steps. The first step of weight loss is observed with 12% weight loss at ~120 °C, due to the vaporization of moisture and liquid elimination of unreacted monomer; the next one (120–300 °C) may be caused by the decomposition of doped acid and aniline oligomer produced in the reaction; and the third one (300–900 °C) is attributed to the complete decomposition of polymer back-bone. For the GO/PANI nanocomposites, exhibit similar decomposition patterns compared with PANI. The total weight loss...
of composites is 55%, the PANI is 63%. In general, the thermal stability of composites is found to be slightly higher as compared to GO.

3.6. Electrochemical Measurement

3.6.1. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was used to study the corrosion behavior of the GO/PANI nanocomposite-based coatings. In the Bode plots, the high-frequency region responds to the protection of the coatings, while the middle and low-frequency region responds to the corrosion reaction between corrosive materials and metal. The Bode plots for the different coatings are shown in Figure 7a. As we know, the $|Z|$ modulus displayed by the Bode diagram at low frequency ($F = 0.01 \text{ Hz}$) is determined to define the corrosion resistance of the coating. Correspondingly, the value of $|Z|_{0.01\text{Hz}}$ for different samples coated steel in 3.5 wt.% NaCl solution was found that increasing in the sequence epoxy $<$ PANI $<$ GO $<$ PG1 $<$ PG2 $<$ PG5 $<$ PG3 $<$ PG4. It can be found that the corrosion resistance with GO, PANI and GO/PANI composites coatings is obviously better than the pure epoxy coatings. For the composite samples, withstanding corrosive competence of the coatings was increased first and then decreased as the GO loadings increased. Compared with all other samples, PG4 displayed the best anti-corrosion performance in 3.5 wt.% NaCl solution.

Figure 7b shows the Nyquist plots of the samples. Generally, the larger the diameter of the Nyquist curve is, the better the corrosion resistance of the sample will be. It shows that the diameters of the Nyquist curve has the same order as that of Bode plots, confirming the consistency of results. The impedance of the coatings is four to five orders of magnitude higher than that of the bare steel. With the increase of GO content in the composites, the coating demonstrates better anti-corrosion performance. However, the performance of the epoxy/PG5 coating decreased slightly, due to the
agglomeration of PANI increased on the surface at higher GO content. In summary, the performance of GO/PANI composites is greater than PANI, GO, epoxy and uncoated coatings.

3.6.2. Potentiodynamic Polarization Studies

Figure 8 shows the potentiodynamic polarization curves of different coatings in 3.5 wt.% NaCl solution, and the values of corrosion potential ($E_{\text{corr}}$), corrosion current ($I_{\text{corr}}$) and corrosion rate (CR) of electrochemical measurements are summarized and shown in Table 1. The value of $I_{\text{corr}}$ and $E_{\text{corr}}$ can be determined via the intersection of the tangent of the anodic and cathodic polarization curves. The CR of the specimens was calculated using the following formula [44]:

$$CR = \frac{KMI_{\text{corr}}}{DV},$$

where $K$ is 3268.5 (mol/A), $M$ is the molecular weight of iron 56 (g/mol), $D$ is the density of iron (7.85 g/cm$^3$) and $V$ is the valence of iron.

![Figure 8. Potentiodynamic polarization curves for the different coatings.](image)

**Table 1.** Tafel plots data for the different coatings.

| Sample           | $E_{\text{corr}}$ (V) | $I_{\text{corr}}$ (A/cm$^2$) | Corrosion Rate (mm/Year) |
|------------------|------------------------|-------------------------------|--------------------------|
| bare steel       | -0.813                 | $3.64 \times 10^{-4}$         | 4.24                     |
| pure epoxy       | -0.704                 | $6.83 \times 10^{-6}$         | $7.96 \times 10^{-2}$    |
| epoxy/GO         | -0.548                 | $1.79 \times 10^{-8}$         | $2.09 \times 10^{-4}$    |
| epoxy/PANI       | -0.569                 | $3.98 \times 10^{-7}$         | $4.64 \times 10^{-3}$    |
| epoxy/PG1        | -0.426                 | $6.72 \times 10^{-8}$         | $7.83 \times 10^{-4}$    |
| epoxy/PG2        | -0.419                 | $2.09 \times 10^{-8}$         | $2.44 \times 10^{-4}$    |
| epoxy/PG3        | -0.375                 | $7.82 \times 10^{-9}$         | $9.12 \times 10^{-5}$    |
| epoxy/PG4        | -0.403                 | $4.68 \times 10^{-9}$         | $5.46 \times 10^{-5}$    |
| epoxy/PG5        | -0.378                 | $1.17 \times 10^{-8}$         | $1.36 \times 10^{-4}$    |

As shown in Table 1, the $E_{\text{corr}}$ value of bare steel is seen to increase from $-0.798$ V for bare steel to more $E_{\text{corr}}$ as $-0.704$, $-0.548$, $-0.569$, $-0.426$, $-0.419$, $-0.375$, $-0.403$, and $-0.378$ V in epoxy-coated, epoxy/PANI, epoxy/GO, epoxy/PG1, epoxy/PG2, epoxy/PG3, epoxy/PG4 and epoxy/PG5 coated samples, respectively. It is obvious that the $E_{\text{corr}}$ of all the coating samples had a positive shift compared with bare steel. $E_{\text{corr}}$ mainly represents the tendency of corrosion reaction, where a sample with the higher $E_{\text{corr}}$ has a better corrosion resistance [45]. Therefore, it can be concluded that the addition of composite material significantly improves its anti-corrosion performance. According to formula (1), the $I_{\text{corr}}$ and corrosion rate are in positive proportion to the relationship. Therefore, the sample with a lower $I_{\text{corr}}$ value will have the lower corrosion rate. Table 1 indicates that the $I_{\text{corr}}$ ranked by numerical value from the largest to smallest: uncoated steel, coatings in epoxy, epoxy/PANI, epoxy/GO, epoxy/PG1, epoxy/PG2, epoxy/PG5, epoxy/PG3 and epoxy/PG4. The corrosion current on
the coated surfaces is apparently much lower (approx. 2–5 orders of magnitude) than the bare steel. It is obvious that coatings with epoxy/PG have better corrosion resistance than epoxy/PANI and epoxy/GO, demonstrating an increase in corrosion resistance of the GO/PANI nanocomposites coated substrates. Meanwhile, the decreased amplitude of corrosion current is positively correlated with the increase of GO content, indicating that GO plays a leading role in nanocomposites. It is easy to determine that the coating with PG5 composites have lower anti-corrosion property than the PG4, it may be that the excessive amount of GO leads to the deterioration of polymer dispersion performance, so that the barrier performance deteriorates. It can be seen that the results of electrochemical impedance spectroscopy are in good agreement with the potentiodynamic polarization. In particular, among all of the coatings, the epoxy/PG4 showed the best anti-corrosion performance and the lowest retained CR (5.46 × 10^{-5} mm/year).

4. Conclusions

GO/PANI nanocomposites with unique anti-corrosion properties were synthesized by in-situ polymerization. Structural analyses were conducted through FTIR, UV–vis, XRD, and TGA to confirm that the PANI successfully synthesis on the surface or interlayers of GO. The epoxy/GO/PANI coatings were prepared to improve the corrosion resistance. The corrosion protection properties of the composite coatings in 3.5 wt.% NaCl solution was tested by potentiodynamic polarization and EIS measurements. Among all the coatings with different samples, the epoxy/PG4 coating shows the best anti-corrosion performance, the |Z|0.01Hz value of which is 12.4 times higher than epoxy/PANI and 55.22 times higher than pure epoxy coating. The composite coating has excellent corrosion resistance because it achieves higher corrosion inhibition efficiency and protection efficiency compared with PANI and epoxy coatings. It is concluded that GO/PANI composite materials can expand the application in the field of anti-corrosion due to their simple preparation, stable performance, and good anti-corrosion effect, etc.

Author Contributions: R.H., S.Y., and S.Z. conceived and designed the experiments; S.Y. and S.Z. performed the experiments; S.Y. and S.Z. analyzed the data; S.Y. and S.Z. conceived the methodology; S.Y. and S.Z. validated the obtained results; S.Y. and S.Z. wrote the manuscripts; R.H. performed review and editing. All authors have read and agreed to the published version of the manuscript.

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