**Anti-Corrosive Coating of Carbon-Steel Assisted by Polymer-Camphorsulfonic Acid Embedded within Graphene**

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**Abstract:** A novel, economic and environmentally friendly anticorrosion coating material for metals is introduced and investigated in this paper. For this purpose, camphor-sulfonic-acid/graphene-doped poly(o-toluidine) composites (MG/CSA@POT) were fabricated using in-situ polymerization with (NH₄)₂S₂O₈ as an oxidant. The structure and the morphology of MG/CSA@POT were analyzed using FTIR (Fourier-transform infrared spectroscopy), XRD (X-ray diffraction), and SEM (Scanning Electron Microscope). Multilayer graphene (MG)/CSA@POT-polyurethane composite coatings (MG/CSA@POT-WPU) were prepared on the surface of a carbon steel substrate by mixing MG/CSA@POT with waterborne polyurethane via blending. The corrosion performance of the MG/CSA@POT-WPU composite coatings in a 3.5% NaCl solution was studied with a corrosion electrochemical method. The results showed that 5-MG/CSA@POT-WPU had the best shielding effect on corrosive media and the lowest corrosion rate (1.02 × 10⁻⁶ mm/year) compared to other coatings while its inhibition efficiency reached 99.96%.

**Keywords:** anticorrosion coating material; corrosion; graphene composite; polymer nanocomposites

**1. Introduction**

Corrosion is an irreversible chemical reaction that is typically accompanied by metal damage. It occurs frequently with many applications of metals, reduces the operating life of metal workpiece and often increases the risk of accidents. Hence, effective protection of metal from corrosion is an important research topic. Organic coatings are commonly used to protect from corrosion; however, they often contain heavy metals such as chromium or lead, which introduces environmental and health concerns. Therefore, it is highly desirable to develop anticorrosion coatings, which are effective, nontoxic and environment-friendly. The invention of polyaniline [1–3], polypyrrole [4–6], polythiophene [7,8], and other polymers offers new solutions to this problem. Polyaniline, in particular, is regarded as one of the most commercially promising materials.

Because of large conjugated Π-bonds in polyaniline molecules, molecular chains are very rigid, which results in low solubility and dispersibility. Through structural modification, substituents can be introduced into the main chain of polyaniline to reduce the rigidity of the molecular chain, which can greatly increase its dispersibility and solubility. This enables the formation of a more uniform and dense protection layer on the surface of the metal to be protected [9–13]. Poly-o-toluidine (POT), which is obtained by structural modification of polyaniline, is a typical example [12]. The ortho position of POT is blocked by a methyl group, which can effectively prevent unintended reactions that may occur at the substitution position. This facilitates the formation of a large conjugated system for the entire molecule.
Furthermore, POT has the characteristic of rapid switching between the reduced state and the oxidized state [14]. This has been a popular research topic [15–17]. Hu et al. [15] added nanotitanium dioxide into hydrochloric acid-doped POT using in-situ polymerization. The resulting POT/nanotitanium dioxide composite coating could effectively reduce the penetration of water and corrosive substances in a 3.5% sodium chloride solution, and its protective efficiency of steel reached 97.85%. Shinde et al. [17] obtained a uniform, dense and highly adherent POT coating on a Cu surface using cyclic voltammetry, which reduced the corrosion rate of copper by a factor of nearly 40.

It was shown that adding graphene as a filler to waterborne coatings can fill defects of resin and effectively delay metal corrosion [18]. The conductive anticorrosive coating (graphene) prepared by Chen et al. [19] had excellent water resistance and neutral salt spray resistance. After a salt spray experiment (1500 h) and immersion in a 3.5% NaCl solution for 60 days, the protective properties of the graphene coating were still good. In addition, Liu et al. [20] and Jiang et al. [21] found that, after being modified by graphene, both the corrosion rate and the corrosion-current density of the film were reduced. The electrochemical impedance spectroscopy also revealed that the ionic-current resistance and the charge-transfer resistance in the hole were improved significantly when a certain amount of graphene was added to the polymer to form the coating. Those results showed the positive effect of graphene-composite coatings with respect to corrosion resistance.

In this study, POT/graphene composites were prepared using in-situ chemical oxidation with camphor-sulfonic acid (CSA) as a doping acid. The polymer nanocomposites were characterized using FTIR and XRD. The microstructures of the samples were also analyzed by SEM. In addition, a POT/graphene-composite coating was prepared using waterborne polyurethane as an adhesive and low carbon steel as a metal substrate. The anticorrosive effect of the composite coating in a 3.5% sodium chloride solution at room temperature was investigated using dynamic polarization and Electrochemical Impedance Spectroscopy.

2. Experimental

2.1. Materials

An o-toluidine monomer was vacuum-distilled, until it was light yellow before use, The other reagents, without special instructions, experienced no additional processing. MG (5–10 layers) was commercially supplied by Jiangsu Hengqiu Technology Co., Ltd., Suzhou, China. o-toluidine, ammonium persulfate (APS), and CSA were purchased from Shanghai Maclean Biochemical Technology Co., Ltd., Shanghai, China. Butanol, dibutyl phthalate, ethyl acetate, and sodium chloride were purchased from Tianjin Komi Chemical Reagent Co., Ltd., Tianjin, China. N-methyl-2-pyrrolidone (NMP) was purchased from Da Mao Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Preparation

One hundred milliliters of 0.05 M o-toluidine was added to 100 mL of 0.05 M CSA, and the mixture was thoroughly stirred to obtain a uniformly mixed solution A. MG (0, 0.03, and 0.05 g), with varying contents, was evenly dispersed in 100 mL double-distilled water to obtain a graphene suspension. Solution A was transferred to the graphene suspension above and stirred continuously for 30 min to obtain mixture B. Mixture B was then transferred to a three-necked flask, and ammonium persulfate (the molar ratio of the o-toluidine monomer to ammonium persulfate was 1:1) was added dropwise by stirring at 150 to 200 rpm, to obtain mixed liquid C. Subsequently, a three-necked flask, which contained mixture C, was placed in a water bath at 5 °C and stirred continuously for 20 h before being filtered. The filtered residue was washed with double-distilled water and pure ethanol, and the washed residue was dried in a vacuum oven at 60 °C for 24 h. Graphene/POT composites, with graphene contents of 0, 0.03, and 0.05 g (labeled as CSA@POT, 3-MG/CSA@POT, and 5-MG/CSA@POT, respectively) [22], were obtained.
The carbon-steel substrate (2 cm × 2 cm) was sequentially and mechanically ground, using 600–2000 mesh sandpaper. The polished carbon-steel surface was washed with acetone and distilled water, dried naturally and stored until use. The composite powder with a mass of 0.25 g was uniformly dispersed in a solution of 0.4 mL of NMP and 0.2 mL of ethyl acetate. Then, 1 g of the waterborne polyurethane was added thereto, and the mixed solution was ultrasonicated, stirred to a certain viscosity and free from bubbles. The as-prepared coating was placed in a natural environment for surface solidification, and then it was placed in an oven at 60 °C, dried and solidified for 1 h to form a stable coating structure. The preparation process of the camphor-sulfonic-acid-doped graphene/poly-o-toluidine-polyurethane composite coating (MG/CSA@POT-WPU) on the surface of the carbon-steel substrate is shown in Figure 1.

![Figure 1. Schematic of the preparation of a camphor-sulfonic-acid-doped graphene/poly-o-toluidine-polyurethane (MG/CSA@POT-WPU) composite coating.](image)

2.3. Characterization

The structure of the powder material was characterized using a Nicolet 6700 Fourier infrared spectrometer from American Thermo Fisher Scientific (wavelength range: 4000 to 500 cm⁻¹, Waltham, MA, USA) and the X Pertpro polycrystalline X-ray diffractometer from the Dutch PANalyco (10°–90° for Cu K-alpha radiation, λ = 0.15406 nm). The morphology of the sample was observed using an Ultra-Plus Zeiss Microscope (Oberkochen, Germany) with an acceleration voltage of 20 kV.

The corrosion resistance test of the coating was analyzed using a Princeton Electrochemical Workstation VersaSTAT 3. The coating samples were electrochemically tested in a 3.5% NaCl solution at room temperature, using a three-electrode system. The carbon steel sample served as the working electrode, and the saturated calomel electrode and the platinum electrode were the reference electrode and the counter electrode, respectively. The scan voltage of the potentiodynamic polarization test had an open-circuit potential of ±200 mV, and the scan rate was 0.001 V/S. Electrochemical Impedance Spectroscopy test was performed in a frequency range of 0.01 to 100 kHz, and the test results were analyzed with ZSimpWin 3.5 software.

3. Results and Discussion

3.1. Structure and Morphology

The infrared spectra of CSA@POT, 3-MG/CSA@POT, and 5-MG/CSA@POT are shown in Figure 2. The absorption doublet, located near 1500–1600 cm⁻¹, was the characteristic peak for the benzoquinone
bimodal structure typical for organic polymers, wherein the absorption peak at 1562.8 cm\(^{-1}\) was attributed to the C=C vibration of the quinone unit and 1586.0 cm\(^{-1}\) was attributed to the C=C vibration of the benzene ring in the POT chain [23,24]. The absorption peaks at 1162.70 and 805.75 cm\(^{-1}\) were ascribed to the plane-stretching vibration of C–H in the quinone ring and the external plane bending vibration of C–H in the benzene ring, respectively. The absorption peaks at 1269.5 and 3224.7 cm\(^{-1}\) were attributed to the stretching vibrations of C–N and N–H, respectively. For graphene, the stretching vibration peak at 3460.2 cm\(^{-1}\) belonged to the O–H bond, and the absorption peak at 1645.5 cm\(^{-1}\) was attributed to C=O or C–OH stretching [25]. Figure 2 shows that 3-MG/CSA@POT and 5-MG/CSA@POT had obvious absorption peaks at 3460.2 cm\(^{-1}\) compared to the infrared absorption spectrum of CSA@POT and the intensity of the absorption peak of 5-MG/CSA@POT was significantly stronger than that of 3-MG/CSA@POT. The appearance of this absorption peak confirmed the successful preparation of the graphene/POT compound.

Figure 2. FTIR spectra of graphene, CSA@POT, 3-MG/CSA@POT, and 5-MG/CSA@POT.

Figure 3 shows the XRD patterns of CSA@POT, 3-MG/CSA@POT, and 5-MG/CSA@POT. Strong diffraction peaks appeared at \(\theta = 14^\circ\) and \(24^\circ\), which indicated that the materials in all 3 composites had a certain degree of crystallinity. In addition, at \(\theta = 20^\circ\), a small, sharp and diffraction peak appeared for both 3-MG/CSA@POT and 5-MG/CSA@POT, which could be due to the structural characteristics of graphene.

Figure 3. XRD spectra of CSA@POT, 3-MG/CSA@POT, and 5-MG/CSA@POT.
3.2. Morphological Characterization of the Composite Powders and Coatings

The SEM images of CSA@POT, 3-MG/CSA@POT, and 5-MG/CSA@POT powders are shown in Figure 4a–c, respectively. The particle sizes of CSA@POT, 3-MG/CSA@POT and 5-MG/CSA@POT tended to decrease. This is mainly because the addition of graphene hindered the increase of the self-assembly of POT, and this blocking effect increased with an increasing amount of graphene. In other words, the addition of graphene helped reduce the particle size of the powder and provided a basis to obtain a dispersed and uniform coating. Figure 4d–f shows the SEM images of CSA@POT-WPU, 3-MG/CSA@POT-WPU, and 5-MG/CSA@POT-WPU coatings applied to the surface of carbon steel. The surface of the CSA@POT-WPU coating in Figure 4d was uneven, with voids and cracks of different sizes. The surface roughness of the 3-MG/CSA@POT-WPU coating (Figure 4e) decreased, and no obvious holes or cracks were observed on the surface. The degree of concavity or convexity of the 5-MG/CSA@POT-WPU coating surface was further reduced, which produced a fine fold structure. These results suggested that the addition of graphene not only reduced the particle size of the material, but also increased its solubility in the resin. The addition of graphene helped improve the uniformity and integrity of the coating and provided a guarantee to enhance the anticorrosion properties of the coating material.

![SEM images of composite coatings](image)

**Figure 4.** SEM images of CSA@POT (a), 3-MG/CSA@POT (b), 5-MG/CSA@POT (c), CSA@POT coating (d), 3-MG/CSA@POT coating (e), and 5-MG/CSA@POT coating (f).

3.3. Analysis of the Corrosion Resistances of the Coatings

The potentiodynamic polarization curves for the bare steel and the samples that were covered with CSA@POT-WPU, 3-MG/CSA@POT-WPU, and 5-MG/CSA@POT-WPU coatings in a 3.5% NaCl aqueous solution are shown in Figure 5. According to Figure 5, both the corrosion potential and the corrosion current were obtained by extrapolation. Then, the corrosion rate was calculated using Equation (1), to compare the protection effect of the composite coating on the substrate more accurately [26]:

\[
C_R = 3270 \times \frac{M(g) \cdot i_{corr}(A/cm^2)}{n \cdot p(g/cm^2)}
\]  

(1)

where \( M \) is the molecular weight of the steel, \( i_{corr} \) is determined by the intersection of the linear portion of the anode and cathode portions of the dynamic polarization curve, \( n \) is the number of electrons lost
during the oxidation reaction, and \( \rho \) is the density of the steel. The values that were calculated via extrapolation are listed in Table 1. In Figure 5 and Table 1, it can be seen that, compared with the bare steel, the self-corrosion potentials of the samples, which were covered with organic coating, shifted more significantly to the right and their corrosion currents also had a greater downward trend. The corrosion potentials of the samples shifted from \(-0.86\) V for the bare steel to \(-0.82\) V for CSA@POT-WPU, \(-0.78\) V for 3-MG/CSA@POT-WPU, and \(-0.67\) V for 5-MG/CSA@POT-WPU. The corrosion current \( (i_{corr}) \) decreased from \(-4.05\) A/cm\(^2\) for the bare steel to \(-5.01\) A/cm\(^2\) for CSA@POTWPU, \(-5.21\) A/cm\(^2\) for 3-MG/CSA@POT-WPU, and \(-5.99\) A/cm\(^2\) for 5-GM/CSA@POT-WPU, where 5-MG/CSA@POT@WPU had the smallest corrosion current. The anticorrosion efficiency of 5-GM/CSA@POT-WPU, calculated using Equation (1), was \(1.02 \times 10^{-6}\) mm/year, 31 times lower than for the bare steel, 10 times lower than for CSA@POT, and 6 times lower than for 3-MG/CSA@POT-WPU. Covering the organic coating material on the surface of the carbon steel reduced the contact rate of the etched ions in the corrosive medium with the metal surface, which increased the corrosion potential, reduced the corrosion current and improved the anticorrosion efficiency. After adding graphene to the coating material, the pores of the CSA@POT itself were filled with graphene, which further reduced the contact rate for the corrosive ions with the surface of the carbon steel. Moreover, due to the filling of the graphene, the diffusion path of the erosion ions in the coating material became more tortuous, which further prevented the carbon steel surface from corrosion by the corrosive medium. The result is consistent with the conclusion in [27] that graphene could improve the corrosion resistance of coatings. Cui [27] proposed the internal corrosion properties of coatings are enhanced because of the synergistic effect of the barrier properties of graphene nanocrystals and polymers.

![Figure 5](image_url)

**Figure 5.** Potentio-dynamic polarization curves for the bare steel, CSA@POT coating, 3-MG/CSA@POT coating, and 5-MG/CSA@POT coating in a 3.5% NaCl solution.

The Electrochemical Impedance Spectroscopy (EIS) curve for the bare steel and samples covered with CSA@POT-WPU, 3-MG/CSA@POT-WPU, and 5-MG/CSA@POT-WPU coatings, after being immersed in a 3.5% NaCl aqueous solution, are shown in Figure 6. The fitted impedance parameters of the bare steel and the coatings, which were obtained by simulating the data with ZSimpWin 3.5 software, are summarized in Table 1. It can be seen that the EIS curves of all samples in Figure 6 are shown as an incomplete semi-arc shape. The impedance radius of the sample piece in Figure 6b followed the order: \( r_{POT} < r_{3-gmp} < r_{5-GMP} \). Generally, the EIS curve for the bare steel at the beginning of the immersion showed two semi-circular arcs. The small semicircular arc within the high-frequency region was attributed to the corroded film formed in the early stage of immersion, while the large semi-circular arc in the low-frequency region was attributed to the corrosion process occurring below
the corrosion film [28]. However, with the increase of the immersion time, the coatings were resolved gradually and finally formed a circle. The fitting circuits, which corresponded to the bare steel and the coated carbon-steel samples, are embedded in Figure 6a,b, respectively. The circuit model comprised solution resistance (Rs), charge transfer resistance (Rct), capacitance, and constant phase components (CPEs). The capacitors Cc and Cdl were coated capacitors and double-layer capacitors on the surface of carbon steel, respectively, while the CPE describes the nonideal capacitance properties. One time constant consisted of CPE1 and Rct in the equivalent circuit for the bare steel, while there were two time constants in the equivalent circuit for the organic coated samples, which were attributed to the protective properties of the organic coatings. The time constant, which included CPE2 and Rct, usually represented the barrier effect between the coating and the substrate. In the equivalent circuit, the high-frequency region corresponded to the electrochemical impedance at the interface between the solution and the coating. Furthermore, the low-frequency region corresponded to the electrochemical resistance between the coating and the substrate. When graphene was added to CSA@POT, the |Z|0.01 radius of 5-MG was larger than for 3-MG/CSA@POT-WPU, which suggested that the 5-MG/CSA@POT-WPU coating had a large charge-transfer resistance (Rct). This meant that the coating had a higher impedance and a lower capacitive reactance. The corrosion inhibition efficiency (IE) of the coating, which was calculated using Equation (2) [29], is shown in Table 1:

\[
IE(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100%
\]  

where \(R_{ct}^0\) and \(R_{ct}\) represent the charge-transfer resistances of the bare steel and the coating, respectively. According to the EIS data, the IE (%) of the polymer coating was calculated as 99%. The 5-MG/CSA@POT-WPU had the best protection effect, and its corrosion inhibition efficiency was 99.96%.

Table 1. Parameters for potentiodynamic polarization and electrochemical impedance spectroscopy in a 3.5% NaCl solution.

| Coatings                  | Potentio-Dynamic Polarization | Electrochemical Impedance Spectroscopy |
|---------------------------|-------------------------------|--------------------------------------|
|                           | \(E_{corr}\) (V) | \(i_{corr}\) (A/cm²) | \(C_R\) (mm/year) | \(R_s\) (Ω·cm²) | \(R_C\) (Ω·cm²) | \(R_{ct}\) (Ω·cm²) | IE (%)       |
| Bare steel                | -0.86                        | -4.50                              | 3.16 × 10⁻⁵ | 18.15            | -              | 1227             | -            |
| CSA@POT-WPU               | -0.82                        | -5.01                              | 9.78 × 10⁻⁶ | 26.20            | 156.9          | 139,630          | 99.12        |
| 3-MG/CSA@POT-WPU          | -0.78                        | -5.21                              | 6.17 × 10⁻⁶ | 28.15            | 247.3          | 869,260          | 99.85        |
| 5-MG/CSA@POT-WPU          | -0.67                        | -5.99                              | 1.02 × 10⁻⁶ | 27.57            | 243.4          | 3.16 × 10⁶       | 99.96        |

Figure 6. (a) EIS curves for the bare steel in a 3.5% NaCl solution. (b) EIS curves for CSA@POT coating, 3-MG/CSA@POT coating, and 5-MG/CSA@POT coating in a 3.5% NaCl solution.
3.4. Mechanism

Although corrosive ions such as H$_2$O, O$_2$, and Cl$^-$ can corrode metals, corrosion can be inhibited by preventing these materials from contact with active metal surfaces such as iron and copper. According to the redox characteristics of POT, when the etched ions were in contact with the polymer, they were converted between polymer$^+$ and polymer$^-$, thereby maintaining the relative stability of the substrate potential [30]. In addition, the addition of a large volume of camphor-sulfonate anions increased the electronegativity of the CSA@POT coating surface and played a role in repelling the anion. This largely avoided the corrosion of the metal surface by the corrosive medium [31,32]. However, the surface of the POT coating was uneven, and there were large pores, which facilitated the diffusion of the ions through the pores to the metal surface, which led to the corrosion and the peeling-off of the coating. When graphene was added, the pores of CSA@POT itself were filled, and the flatness of the coating surface was improved to form a dense and compact surface structure. Thus, this can reduce the diffusion of corrosive substances into the active metal substrate. It can be further illustrated from Figure 7 that the addition of graphene can improve the corrosion resistances of the coatings. It can be found after peeling off the coatings, the surface roughness of the carbon steel, coated with the doped-graphene, was significantly lower than that of the carbon steel that was coated with the CSA@POT-WPU coating. In addition, the corresponding surface porosity was also reduced significantly. In particular, the carbon-steel surface, coated with 5-MG/CSA@POT-WPU, still maintained a relatively tight structural state. It was suggested that the coating material, which was doped with graphene, could produce a better anticorrosion effect, and 5-MG/CSA@POT-WPU had a stronger protection effect on the surface of carbon steel.

![SEM images after peeling off the coatings: (a) CSA@POT coating; (b) 3-MG/CSA@POT coating; (c) 5-MG/CSA@POT coating.](image1)

**Figure 7.** SEM images after peeling off the coatings: (a) CSA@POT coating; (b) 3-MG/CSA@POT coating; (c) 5-MG/CSA@POT coating.

On the other hand, the adhesion between the coating and the substrate was increased by adding graphene to the CSA@POT matrix, and the resistance to long-term corrosion in corrosive environments was enhanced. The corrosion protection mechanism of CSA@POT and MG/CSA@POT coatings is shown in Figure 8a,b, respectively.

![Corrosion protection mechanisms (a) CSA@POT (b) MG/CSA@POT.](image2)

**Figure 8.** Corrosion protection mechanisms (a) CSA@POT (b) MG/CSA@POT.
4. Conclusions

A CSA/graphene-doped POT composite (MG/CSA@POT) was successfully synthesized using in-situ polymerization, which can be used to protect carbon-steel from the corrosion of 3.5% NaCl solution. The successful preparation and the structural properties of the composites were confirmed by FTIR and XRD analysis. Potentiodynamic polarization and electrochemical impedance spectroscopy measurements were used to monitor the properties of the MG/CSA@POT coating as a corrosion barrier. The addition of MG reduced the pore defects of the CSA@POT-WPU, which improved the corrosion resistance of the composite coating. In the anticorrosion test, the protection efficiency of the 5-MGP coating in a 3.5% NaCl solution reached over 99%. This was mainly due to the inherent properties and multiple-barrier properties of POT. Moreover, 5-MGP can be produced using a simple method. As a result, we believe that this material can be commercialized in the near future.

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