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Preparation of aniline trimer modified graphene oxide new composite coating and study on anticorrosion performance

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Abstract

Graphene oxide (GO) has attracted much attention in anticorrosive coating applications due to its excellent mechanical properties, thermochemical stability and large specific surface area. In this paper, aniline trimer modified GO composites (ATGO) were prepared through modifying GO at different temperatures of 65 °C, 80 °C, 95 °C, and 110 °C, respectively. Aniline trimer modified GO composite coatings (ATGO/EP) were then prepared by adding different quantities of ATGO to epoxy coating, with the mass fractions of 0.05%, 0.1% and 0.3%, respectively. The resulting composite coatings were then sprayed onto Q235 steel plates for characterization and anticorrosion testing. A series of characterization methods such as x-ray diffraction (XRD), Raman spectra, Fourier transform infrared spectroscopy (FT-IR), Atomic force microscopy (AFM) and Transmission electron microscopy (TEM) were used to prove that aniline trimer was successfully grafted on GO. The optimal reaction temperature for ATGO preparation was determined to be 95 °C. Using anticorrosive tests such as Electrochemical impedance spectroscopy (EIS), salt spray test and adhesion test, it was proven that the addition of ATGO can significantly promote anticorrosion performance of epoxy resin (E-44). The optimal addition amount of ATGO to prepare composite coatings was determined to be 0.05 wt%. Its coating resistance after soaking in 3.5% NaCl solution for 10 days was 6.87 × 10⁶ Ω, which was two orders of magnitude higher than the 3.89 × 10³ Ω of pure epoxy coating. The importance and originality of this study is that it explores an effective way to improve the anticorrosion performance of epoxy coatings.

1. Introduction

Many techniques are used for protecting metal against corrosion. Common methods include corrosion inhibitors, cathodic and anodic protection, coating protection and rational selection of materials. Among them, coating protection is generally regarded as the most economical and effective anticorrosion technique [1, 2]. For coating protection, organic coatings are widely used in metal protection because it can well prevent the corrosion of metal materials from the external environment [3–5]. However, in practical application, the organic coatings can not meet the increasing anticorrosion demand for metal materials in the current engineering environment due to their poor anti-permeability and crack resistance [6]. Therefore, a variety of fillers with excellent functions have been developed to improve the barrier properties of organic coatings [7–9].

Graphene is a new type of nanomaterial with excellent performance. As a filler, graphene can improve the corrosion resistance, electrical conductivity, mechanical properties and thermal properties of organic coatings [10, 11]. By stacking layers of graphene, it can form a physical barrier, that extends the invasion path of corrosion mediums to metal substrate and delay the corrosion rate of metal [12]. It has already become a hotspot in the research of anticorrosion fillers. In practice, however, due to the Van Der Waals force between graphene layers and the super large specific surface area, graphene easily agglomerates [13–15], and has difficulty dispersing to

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form an effective membrane inside a coating. Therefore, graphene often needs to be modified and optimized by functionalization before application [16–19]. While GO, as a derivative of graphene, has the various advantages of graphene and its surface has many functional groups such as carboxyl group, hydroxyl group, carbonyl group, epoxy group and so on. It is relatively easy to modify and has become the first choice for modification treatment of graphene [20, 21]. Relevant studies have explored materials, including silane coupling agent [22], vinyl triethoxysilane [23], long-chain silicone [24], hyperbranched polyester [25], isophorone diisocyanate [26], and others, in order to discover the best anticorrosion effect of GO in organic coatings.

In recent years, with the awareness of strong chemical bond between amino and epoxy groups, related research tends to use amino covalent bonds to improve the dispersion of GO. Ramezanzadeh et al [27] functionalized GO with phenylenediamine, and then dispersed the modified GO into epoxy resin using a wet transfer method. Its electrochemical impedance of composite coating was $3.16 \times 10^7 \Omega \text{ cm}^2$ after 40 d of immersion test. Yu et al [28] functionalized GO with 3-aminopropyltriethoxysilane, mixed it with water-based epoxy resin, and cured it to form a composite coating. The electrochemical impedance of the composite coating after 14 d immersion test was $5.86 \times 10^6 \Omega \text{ cm}^2$, its corrosion resistance was not improved significantly. Xiong [29] also used 3-aminopropyltriethoxysilane to functionalize salicylaldehyde @ZIF-8 / GO nanoflakes, which improved the compatibility of nano flakes with epoxy resin. The modified nanoflakes after a 20d settlement test still had good dispersion stability in epoxy resin. Palaniappan et al [30] used octylamine-functionalized GO materials as a filler to prepare anticorrosion coatings, and studied the protective effect of composite coatings on metal alloys in 3.5% NaCl medium. which improved the corrosion inhibition performance of metal alloys by 73%. Lu et al [31] combined 3-aminobenzenesulfonic acid and oligoanilines to prepare GO-based sulfonated oligoanilines coatings for marine corrosion protection application, the coating resistance was from 2882 $\Omega \text{ cm}^2$ to $1.419 \times 10^7 \Omega \text{ cm}^2$. Li et al [32] functionalized GO with 10-phenanthroline-5-amine, and studied the corrosion resistance of modified GO / waterborne polyurethane composite coating by observing the red complex formed by the reaction of modified GO with Fe$^{2+}$. Yadav et al [33] found that the addition of GO enhanced the corrosion inhibition performance of amino acids grafted on the surface of metallic iron. Later, by observing the physical arrangement and microscopic morphology of the coating, it was determined that the enhanced performance was due to the connection between the added GO and the corrosion inhibition layer such as para-aminobenzoic acid, glycine, or alanine.

In order to further explore the potential of amino modified GO as a filler to improve the anticorrosion performance of organic coatings, aniline trimer was used as a modifier to form a covalent bond between its terminal amino group and the carboxyl and epoxy group of GO to prepare amino-functionalized GO [34]. Then the amino groups on the surface of the modified GO reacted with the epoxy groups on the edge of epoxy resin to fix GO in the epoxy resin to make anticorrosive coatings. Finally, the composite coatings were sprayed onto Q235 steel plates. The optimal temperature for grafting modification and the optimal addition amount of aniline trimer were analyzed through characterization methods including XRD, Raman spectra, FT-IR, AFM, TEM, EIS, salt spray test and adhesion test, in order to ascertain the optimal modification process of aniline trimer to GO.

2. Experimental

2.1. Materials and reagents

In this paper, the film-forming material of the coating adopts epoxy resin (E-44), the curing agent adopts polyamide resin (PA650), the diluent adopts n-butanol/xylene mixed solution, and the coating spray sample adopts a Q235 steel plate. The composition of the Q235 steel plate is shown in table 1. Graphene oxide was purchased from Dasheng Graphite New Materials Co., Ltd. Aniline trimer was purchased from Shanghai Macklin Biochemical Co., Ltd. Epoxy resin and polyamide resin were purchased from Feicheng Deyuan Chemical Co., Ltd. Xylene was purchased from Tianjin Jindong Tianzheng Fine Chemical Reagent Factory. N-butanol was purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd.

2.2. Synthesis of ATGO

ATGO composites were prepared at temperatures of 65 °C, 80 °C, 95 °C, and 110 °C respectively. The preparation steps were as follows: 0.25 g of Go was dissolved in 100 ml of ultrapure water, mixed and stirred

| Table 1. Chemical composition of Q235 steel plate (wt%). |
|----------------|---------------|-------------|-------------|-------------|-------------|---------------|
| Fe             | Mn            | Si          | P           | S           | C           |
| Balance        | 0.47          | 0.28        | 0.033       | 0.047       | 0.17        |
evenly, and then ultrasonic treated at room temperature for 30 min. Next, 0.1 g of aniline trimer was dissolved in 20 ml of ultrapure water to prepare a solution (5 mg ml$^{-1}$). To produce ATGO, the aniline trimer solution and GO solution were mixed at a mass ratio of 1:5, and stirred at their respective temperatures for 30 min using a thermostatic magnetic water bath agitator. Afterwards the ATGO solution was poured into an evaporating dish and dried in a thermostatic air-blower-driven drying closet for 24 h. After the ATGO was completely dried, it was ground into powder and loaded into a collection tube for subsequent experiments. The modified GO composites were named ATGO65, ATGO80, ATGO95 and ATGO110, to indicate their respective preparation temperatures.

### 2.3. Synthesis of ATGO/EP

ATGO/EP composite coatings were prepared with mass fractions of ATGO at 0.05%, 0.1% and 0.3% respectively. The preparation steps were as follows: ATGO at the specified mass fractions above was first dissolved in water and treated with ultrasound at room temperature for 30 min. Then the evenly mixed dispersion was mixed with epoxy resin. Ultrasound treatment was continued for another 30 min. After the epoxy was well mixed with the modified GO, it was dried to remove excess water and heated at 100 °C for 48 h to completely evaporate the water in the mixture. A mixture of xylene and n-butanol (mass ratio 7:3) was then prepared as a diluent. The evaporated epoxy resin mixture was mixed with the curing agent polyamide resin (mass ratio 10:7), and its viscosity was adjusted by the above mixture of xylene and n-butanol until spraying viscosity was achieved. Q235 steel plates were cleaned with acetone to remove surface oil stains, then the surface of the steel plate was polished with 400 mesh, 800 mesh and 1200 mesh sandpaper successively. The surface of the steel plate was cleaned again with acetone to remove metal particles attached to the surface of the steel plate, then when dried, the prepared composite coatings were sprayed onto the surface of the steel plates. Finally, the coating was dried in an oven at 80 °C for 24 h and the thickness of the coating was controlled within 30 ± 5 μm. In addition, the same experimental process and conditions above were repeated using a pure epoxy coating as a blank control group. The Schematic illustration of epoxy resin chains bonding to the ATGO surface is shown in figure 1.
2.4. Characterization

2.4.1. Chemical characterization

The crystal structures of GO and ATGO were characterized using x-ray diffraction (XRD, D/ Max-2500/PC, 30 kV, 35 mA, CuKα) with a scanning range of 5°–57° and a scanning rate of 3° min⁻¹. A Raman spectrometer (HORIBA IHR 320) was used to characterize the defect and crystallization degrees inside the sample. The laser wavelength was 532 nm, and the scanning range was 100–4000 cm⁻¹. The changes in the surface functional groups of the samples were characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker, TENSOR II). KBr was used as the dispersion medium of the samples, and the wavenumber range was 500–4000 cm⁻¹. The surface morphology of the samples was characterized by Atomic force microscope (AFM, Bruker, MultiMode8) and Transmission electron microscope (TEM, JEM2100) at 200 kV accelerating voltage.

2.4.2. Corrosion performance tests

In corrosion study, the corrosion resistance of epoxy coating and ATGO/EP composite coating samples were evaluated by Electrochemical impedance spectroscopy, salt spray test and adhesion test. The type of electrochemical workstation used for the Electrochemical impedance measurement was PMC-1000A of Princeton. A three electrode system was used in the experimental system, that is, metal platinum electrode as the counter electrode, saturated calomel electrode as the reference electrode and anticorrosive coating as the working electrode. The surface area of the working electrode was 1 cm², and the electrolyte was 3.5% sodium chloride solution. The frequency test range of the AC impedance spectrum was 100 kHz–10 mHz, the amplitude was 20 mV, the scanning rate was 1 mV s⁻¹, and the voltage of polarization curve test was within the range of ±250 mV. The type of test chamber used in the salt spray test was YWX-150. The brine concentration was 5 mg ml⁻¹, the PH value of the salt solution was between 6.5–7.2, the test temperature was 35 °C, and the saturator temperature was between 35 °C–40 °C. The pull-out apparatus used in the adhesion test was Defelsko, with a drawing speed of 0.5 MPa s⁻¹ and a spindle size of 20 mm.

3. Results and discussion

3.1. Characterization of GO and ATGO

3.1.1. x-ray diffraction

By means of XRD spectra, the interlayer spacing between GO and ATGO was analysed to explore the reaction between amino and GO surface functional groups. The XRD spectra of GO and modified GO are shown in figure 2. For the characteristic peak of GO (001), according to the Bragg equation (1).

\[
2d \sin \theta = \lambda
\]

Where, \(d\) is the interlayer spacing of GO or modified GO; \(\theta\) is the grazing angle; \(\lambda\) is the x-ray wavelength. It can be calculated that the interlayer spacing of the unmodified GO is 0.65 nm. Similarly, it can be seen from figure 2 that the characteristic peaks of ATGO65, ATGO80, ATGO95, and ATGO110 appear at \(2\theta = 13.2°, 2\theta = 13.2°, 2\theta = 12.3°\) and \(2\theta = 12.8°\), respectively. The interlayer spacing is calculated to be 0.67 nm, 0.67 nm, 0.72 nm and 0.69 nm. Compared with GO, the interlayer spacing of all the modified GO samples was improved by varying degrees. Among them, the interlayer spacing of ATGO95 samples reached 0.72 nm, an increase of about 11%, indicating that aniline trimer had the best modification effect on GO when the reaction temperature was 95 °C. The significant increases in the interlayer spacing indicate that the chemical reaction between the amino
groups and the epoxy groups of GO occurred and that some functional groups and long chains of macromolecules were grafted on the surface of GO, making the interlayer spacing larger [35].

In order to eliminate the influence of other external factors on the characteristic peak shift of modified GO, nano silica powder with a mass fraction of 20% was added to GO and each modified GO sample powder in this study. By comparing silicon characteristic peaks in PDF standard card, it can be concluded that (111) and (220) crystal faces at positions $2\theta = 28.44^\circ$ and $2\theta = 47.30^\circ$ are the characteristic peaks of silicon. The silicon characteristic peaks of GO and each modified GO sample coincides exactly with the characteristic peak of standard silicon. Therefore, it can be inferred that the shift of the (001) characteristic peak of GO was only caused by the internal structure of amino modified GO in aniline trimer, without interference from other external factors.

3.1.2. Raman spectra
To further verify the modification effect of aniline trimer on GO, the Raman spectra of each modified GO sample were measured as shown in figure 3. As can be seen from figure 3, the D peak of GO appears at 1345 cm$^{-1}$ and the G peak appears at 1583 cm$^{-1}$. Through calculating the ratio of integral areas values of D and G peaks, $\frac{ID}{IG} = 1.98$ of GO sample was obtained. After modification at different reaction temperatures, the modified GO samples showed D peak and G peak in the vicinity of 1345 cm$^{-1}$ and 1583 cm$^{-1}$ respectively, indicating that the modification of GO by aniline trimer did not destroy its original lattice structure. Through calculating, the $\frac{ID}{IG}$ values of ATGO65, ATGO80, ATGO95 and ATGO100 were 2.66, 2.37, 3.26 and 2.84, respectively, which showed different degrees of improvement compared with GO, indicating that the internal disorder of GO was enhanced after modification treatment. Analysis suggests that chemical reaction between the amino groups on the aniline trimer and the carboxyl and epoxy groups on the GO formed a new chemical bond, which increased the overall internal disorder of the modified GO. In addition, when the modification temperature was 95 $^\circ$C, the ratio of ID to IG reached the peak value, and the overall structure disorder of modified GO reached its maximum.
value. Therefore, it can be further concluded that the optimum temperature for modification of GO by aniline trimer is 95 °C.

3.1.3. Fourier transform infrared spectroscopy
It can be seen from figure 4 that the characteristic peaks near 3379 cm⁻¹, 1730 cm⁻¹, 1500 cm⁻¹ and 1049 cm⁻¹ correspond to the O–H, C=O, C–N and C–O vibration bands, respectively. Among them, the characteristic peak of 1730 cm⁻¹ corresponds to the vibration of the carboxyl group. Compared with GO, the FT-IR spectra of modified GO showed a significantly lower adsorption strength near 1730 cm⁻¹.

According to the analysis, the reaction between the amino groups on the surface of the aniline trimer and the carboxyl groups on the edge of the GO produced ammonium carboxylate, which led to a decrease in the adsorption strength of the carboxyl groups. Based on the reduction of carboxyl (C=O) characteristic peak strength and the formation of new characteristic peak C–N bond (at 1500 cm⁻¹) in the FT-IR spectra of the
modified GO samples, it can be inferred that the grafting modification of GO was successfully carried out by aniline trimer. In addition, the transmittance of ATGO65, ATGO80, ATGO95 and ATGO110 were 88%, 90%, 82% and 90% respectively after normalization processing. It is generally believed that the lower the transmittance is, the higher the strength of the functional group at this location will be. When the modification temperature was 95 °C, the transmittance of modified GO sample reached the lowest value. The results show that when the modification temperature is 95 °C, aniline trimer has the best modification effect on GO, which is
consistent with XRD and Raman spectra analysis. Therefore, the following characterization is done for the composites obtained at 95 °C.

3.1.4. Atomic force microscopy

The microstructure of GO and modified GO were observed by AFM, as shown in figure 5. As can be seen from figures 5(a) and (d), no obvious agglomeration occurred before or after modification, and the modified GO was more evenly dispersed in the substrate. One of the GO and modified GO sheets were selected to further observe their micromorphology. The layered structure characteristics could be clearly seen, as shown in figures 5(b) and (e). Comparative analysis of the thickness data shows that the lamellar thickness of GO is about 1.169 nm, while the lamellar thickness of modified GO is 1.236 nm, as shown in figures 5(c) and (f).

According to the analysis, compared with the original GO sheet, the slightly increased thickness of the modified GO sheet is due to the aniline trimer grafted some functional groups and macromolecular chains on the surface of GO, which changed the surface functional group structure of the original GO and further increased its thickness. Therefore, it can be proved that aniline trimer has been successfully grafted on GO [36].

3.1.5. Transmission electron microscopy

The micromorphology of GO and modified GO was further observed by TEM, as shown in figure 6. As can be seen from figure 6(a), the surface of GO is relatively smooth and has obvious corrugated folds. After high magnification of the edges, the layered structure of GO can be clearly seen, as shown in figure 6(b). In figure 6(c), after the modification of aniline trimer, the corrugated folds on the modified GO surface were significantly increased and the lamellar thickness was also increased. In figure 6(d) at high magnification, the layered structure can still be clearly seen. It can be proved that the layered structure of the original GO was not damaged after grafting modification of aniline trimer. Therefore, it is feasible to improve the permeability and corrosion resistance of the anticorrosive coatings by utilizing the shielding effect of the modified GO [37].

3.2. Corrosion Study of EP and ATGO/EP

3.2.1. Electrochemical impedance spectroscopy test

At present, a commonly used test method to compare the corrosion resistance of coatings is to soak the coating samples in brine for a period of time, and then compare the EIS and potentiodynamic polarization curve of each coating sample with an electrochemical workstation. In this study, to confirm that the sample maintains a steady state, the OPC curves (figure 7) of each coating sample were measured for 30 min before the EIS test. The Bode and Nyquist plots (figure 8) and the potentiodynamic polarization curves (figure 10) of each coating sample were measured after soaking each coating sample in 3.5% NaCl solution for 10 d, so as to evaluate the corrosion resistance of each coating.

The OCP curves for all samples are relatively steady during 30 min of measurement. In general, the higher the steady state potential in the OCP curve, the better the corrosion resistance of the coating. As can be seen from figure 7, 0.05% ATGO/EP has the highest potential, followed by 0.1% ATGO/EP and 0.3% ATGO/EP, and pure epoxy coating has the lowest potential. The composite coating has the best corrosion resistance when the addition amount of ATGO composites is 0.05 wt%. It is also indicating that excessive addition can cause agglomeration and reduce corrosion resistance.

The original sample Bode plots of each coatings are shown in figure 8(a). Generally, the higher the low frequency (0.01 Hz) corresponding impedance modulus values in the Bode plot, the better the corrosion resistance of the coating. As can be seen from figure 8(a), the impedance value at 0.01 Hz from large to small is:
The smaller the $I_{corr}$ is, the greater the polarization of the potentiodynamic polarization curve diagram, the corrosion current density can represent the actual corrosion resistance. Whether compared with pure epoxy coating or other ATGO composite coatings, the 0.05% ATGO composite coating sample has the largest capacitance arc, and the arc of pure epoxy coating is almost invisible, indicating that the composite coating has the best corrosion resistance when the addition amount of ATGO composite material is 0.05 wt%. The Nyquist plots of the original samples of each coating are shown in figure 8(b). The larger the radius of the curves arc (radius of capacitance arc), the larger the impedance, the smaller the corrosion current, and the better the corrosion resistance. Whether compared with pure epoxy coating or other ATGO/EP coatings, the 0.05% ATGO/EP composite coating sample has the largest capacitance arc, and the arc of pure epoxy coating is almost invisible, indicating that the composite coating has the best corrosion resistance when the addition amount of ATGO composites is 0.05 wt%, which is consistent with the conclusion obtained from the Bode plot.

To investigate the behavior of coatings, considering different time constants, two types of electrical equivalent circuit (EEC) model as shown in figure 9 were fitted to the impedance data obtained and the elements of the circuit were correlated to the electrochemical reactions of the system [27]. In the Nyquist plot, the larger the radius of the curves arc (radius of capacitance arc), the larger the impedance, the smaller the corrosion current, and the better the corrosion resistance. Whether compared with pure epoxy coating or other ATGO/EP coatings, the 0.05% ATGO/EP composite coating sample has the largest capacitance arc, and the arc of pure epoxy coating is almost invisible, indicating that the composite coating has the best corrosion resistance when the addition amount of ATGO composites is 0.05 wt%, which is consistent with the conclusion obtained from the Bode plot.

Table 2. Parameters of equivalent circuits.

| Sample            | $R_p/\Omega$ | $CPE_a$ Y$_0$/Mho | n | $R_n/\Omega$ | $CPE_M$ Y$_0$/Mho | n | $W_0$ Y$_0$/Mho |
|-------------------|--------------|-------------------|---|--------------|-------------------|---|-----------------|
| EP                | 3.89 × 10$^4$ | 690 × 10$^{-9}$   | 0.628 | 1.34 × 10$^5$ | 11.9 × 10$^{-6}$ | 0.424 | — |
| 0.05% ATGO/EP     | 6.87 × 10$^5$ | 444 × 10$^{-12}$ | 0.923 | — | — | — | 39.1 × 10$^{-9}$ |
| 0.1% ATGO/EP      | 1.48 × 10$^5$ | 23.3 × 10$^{-9}$ | 0.856 | 8.29 × 10$^6$ | 195 × 10$^{-9}$ | 0.571 | — |
| 0.3% ATGO/EP      | 1.21 × 10$^5$ | 11.6 × 10$^{-9}$ | 0.684 | 5.23 × 10$^6$ | 333 × 10$^{-9}$ | 0.359 | — |

0.05% ATGO/EP > 0.1% ATGO/EP > 0.3% ATGO/EP > EP, the change rule of the impedance value of the coating with different added amounts at 0.01 Hz is that the impedance value first rose and then fell, and the maximum value appeared at 0.05 wt%. The 0.05% ATGO/EP with the highest impedance is about 2 orders of magnitude higher than the 0.03% ATGO/EP with the lowest impedance, indicating that the composite coating has the best corrosion resistance when the addition amount of ATGO composite material is 0.05 wt%. The Nyquist plots of the original samples of each coating are shown in figure 8(b). In the Nyquist plot, the larger the radius of the curves arc (radius of capacitance arc), the larger the impedance, the smaller the corrosion current, and the better the corrosion resistance. Whether compared with pure epoxy coating or other ATGO/EP coatings, the 0.05% ATGO/EP composite coating sample has the largest capacitance arc, and the arc of pure epoxy coating is almost invisible, indicating that the composite coating has the best corrosion resistance when the addition amount of ATGO composites is 0.05 wt%, which is consistent with the conclusion obtained from the Bode plot.

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To investigate the behavior of coatings, considering different time constants, two types of electrical equivalent circuit (EEC) model as shown in figure 9 were fitted to the impedance data obtained and the elements of the circuit were correlated to the electrochemical reactions of the system [27]. In figure 9, EIS curves of EP, 0.1% and 0.3% ATGO/EP were fitted according to figure 11(a). EIS curves of 0.05% ATGO/EP were fitted according to figure 9(b). $R_s$, $R_{cp}$, $CPE_a$, $CEP_M$, $W_0$ are the solution resistance, coating resistance, charge transfer resistance, constant phase element of the coating, constant phase element of double layer and Warburg element (open), respectively. The circuit elements values obtained after fitting of EEC models are presented in table 2. As can be seen from table 2, compared with pure epoxy coating, the resistance of composite coating was significantly increased. However, the resistance of composite coating did not increase with the increase of the addition of ATGO. Instead, it showed the best performance when the addition amount of ATGO was 0.05 wt%, with the coating resistance up to 6.87 × 10$^6$ Ω. This is probably because the excessive addition of ATGO, which results in the agglomeration of ATGO in the coating, which reduces the barrier effect of the coating on corrosive media.

The potentiodynamic polarization curve diagram, the corrosion current density can represent the actual corrosion current generated in the electrochemical reaction. The smaller the $I_{corr}$ is, the greater the polarization resistance is, indicating the better the corrosion resistance is. We can obtain corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) by fitting the potentiodynamic polarization curves. The corrosion rate (CR) is calculated according to equation (2):

$$CR = \frac{1}{A} \times I_{corr}$$
Where, $K$ is a constant, $3268.5$, $M_m$ is the relative molecular mass ($\text{g/mol}$), $\rho_m$ is the density of the sample ($\text{g/cm}^3$), and CR is the corrosion rate ($\text{mpy}$). The polarization resistance ($R_p$) is obtained according to equation (3):

$$R_p = \frac{\beta_a \beta_b}{2.303 (\beta_a + \beta_b) I_{\text{corr}}}$$

Where, $\beta_a$ and $\beta_b$ are the Tafel slope of the cathode and anode and $R_p$ is the polarization resistance ($\Omega \cdot \text{cm}^2$). The results of the fitting and calculation are shown in table 3. As can be seen from figure 10 and table 3, the absolute value of $E_{\text{corr}}$ and $R_p$ of the anticorrosion coating with ATGO composite increased compared with the pure epoxy coating, the $I_{\text{corr}}$ and CR decreased. However, with the increase of ATGO content, the $I_{\text{corr}}$ and CR increased gradually, and the $R_p$ decreased gradually. The $I_{\text{corr}}$ value of the pure epoxy coating was $4.69 \times 10^{-8} \text{A cm}^{-2}$, and the $I_{\text{corr}}$ value of the 0.05% ATGO/EP composite coating was only $5.21 \times 10^{-10} \text{A cm}^{-2}$, which was about two orders of magnitude lower than that of the pure epoxy coating sample. The $R_p$ of the pure epoxy coating was $4.76 \times 10^8 \Omega$, and the $R_p$ of the 0.05% ATGO/EP composite coating was $2.92 \times 10^{10} \Omega$, which was about two orders of magnitude higher than that of the pure epoxy coating.

It can be concluded that ATGO obtained by modifying GO with aniline trimer can significantly improve the corrosion resistance of composite coating, and when the addition amount of ATGO composites is 0.05 wt%, the corrosion resistance of composite coating can be most significantly enhanced.

### 3.2.2. Salt spray test

In order to verify the actual corrosion resistance of each coating sample, the salt spray corrosion test was conducted for 300 h on each coating sample according to the current national test standard. The results are shown in figure 11. By comparing figures 11(a)–(d), it can be seen that a large number of corrosion spots appeared on the pure epoxy coating samples, the scratches showed obvious corrosion expansion, and a large number of reddish-brown corrosion products (ferric oxide) and black corrosion products (ferroferric oxide) were generated. The corrosion on the pure epoxy coating samples was the most serious. However, the number of

| Samples          | $E_{\text{corr}}$ (mV) | $I_{\text{corr}}$ (A cm$^{-2}$) | CR (mpy) | $R_p$ (Ω) |
|------------------|------------------------|---------------------------------|----------|-----------|
| EP               | $-447.90$              | $4.69 \times 10^{-8}$           | $2.18 \times 10^{-2}$ | $4.76 \times 10^8$ |
| 0.05% ATGO/EP    | $-552.22$              | $5.21 \times 10^{-10}$          | $2.39 \times 10^{-4}$ | $2.92 \times 10^{10}$ |
| 0.1% ATGO/EP     | $-450.27$              | $1.55 \times 10^{-9}$           | $7.26 \times 10^{-4}$ | $1.00 \times 10^{10}$ |
| 0.3% ATGO/EP     | $-487.02$              | $1.58 \times 10^{-9}$           | $7.32 \times 10^{-4}$ | $9.79 \times 10^9$ |

Figure 11. Salt spray test results of (a) EP, (b) 0.05% ATGO/EP, (c) 0.1% ATGO/EP and (d) 0.3% ATGO/EP.
corrosion spots on the surface of the 0.05% ATGO/EP coating samples was significantly reduced, with the corrosion expansion of the scratches was also reduced. Only reddish-brown ferric oxide was produced, and the corrosion degree was the lowest. With the increase of the concentration of aniline trimer, the corrosion spots of the 0.1% ATGO/EP and 0.3% ATGO/EP coating samples began to increase, the corrosion expansion of the scratches was more serious, and the corrosion resistance of the composite coating decreased. After stripping each coating, the corrosion of each metal substrate was compared, as shown in figures 11(e)–(h). As can be seen from figure 11(e), the surface gloss of the metal substrate is the dimmest, a large number of circular speckle corrosion traces appeared at the scratch, and the metal base was seriously corroded. As can be seen from figures 11(f)–(h), the number of corrosion spots on the surface of the three composite coating samples decreased significantly, and there were almost no traces of corrosion at the scratch. The surface of the three metal substrates also still has a degree of metal gloss. This can be explained by the fact that the corrosive medium did not penetrate the coating to the substrate to cause corrosion, and that aniline trimer modified GO as a filler significantly increased the shielding effect of coating on corrosion medium.

3.2.3. Adhesion test
Adhesion is a key property of coatings. The coating will be subjected to greater tests in corrosive environments, once the coating is damaged or even falls off, the corrosive medium will directly contact with the metal substrate. In this study, the dry adhesion (without any immersion) and wet adhesion (after a certain concentration of brine immersion or salt spray test) of the four groups of composite coating samples were compared respectively, as shown in figure 12.

As can be seen from figure 12(a), the dry adhesion of the three composite coatings with modified GO was slightly improved comparing with the dry adhesion of pure epoxy coating, and the coating adhesion did not decrease sharply due to the agglomeration of modified GO, which provided an important guarantee for the anticorrosion performance of the composite coating. By comparing the wet adhesion of each coating, it can be seen that when the three coatings were immersed in 3.5% NaCl solution for 360 h, the wet adhesion of 0.05% ATGO/EP composite coating samples was significantly higher than that of the other two groups, which is about
1.64 times that of the pure epoxy coating. By comparing and analyzing the adhesion loss of the four groups of coatings in figure 12 (b), After the four groups of coatings were immersed in 3.5% NaCl solution for 360 h, the adhesion loss of pure epoxy coating was the largest, up to 81%, followed by the 0.3% ATGO/EP composite coating with 79%, then the 0.05% ATGO/EP composite coating with only 67%. Analysis suggests that the expansion path of the corrosive medium in the coating was significantly increased due to the addition of modified GO composites. Thus, the penetration of corrosive media is effectively blocked and the adhesion between coating and metal substrate is improved.

3.3. Corrosion protection mechanism of ATGO/EP

Based on the above discussion, compared with the epoxy coating, aniline trimer modified GO composite coating can more effectively inhibit the diffusion of corrosive medium and improve the corrosion resistance of the coating. Its anticorrosion mechanism is shown in figure 13.

First of all, when GO is used as a filler alone in epoxy coating, it is very easy for GO sheet to agglomerate due to its super large specific surface area and strong Van Der Waals force. This causes GO to fail to form a good barrier against corrosive mediums. At the same time, there are a large number of hydrophilic groups on the surface of GO, such as carboxyl and hydroxyl groups, which have good compatibility with water, while the epoxy resin is hydrophobic due to the presence of epoxy groups, which leads to the poor compatibility between GO and epoxy resin. Furthermore, in corrosive environment, the epoxy coating will produce cracks and crack diffusion. The corrosive medium may penetrate through these cracks to the interior of the coating and all the way to the interface of the metal substrate, thus reducing the adhesion of the coating and leading to the corrosion of the metal substrate. The aniline trimer, however, can connect the GO sheet with the epoxy resin through its own amino group, greatly improving the dispersion and compatibility of GO in epoxy resin. At the same time, functionalized GO sheets can block the formation of defects and pores and prolong the time it takes for the corrosive media to reach the metal substrate.

In addition, the functional groups on the surface of GO have a certain adhesion to the metal substrate, which can improve the bonding strength between the coatings and the metal substrate. In fact, the epoxy coating itself has a certain adhesion to the metal substrate, but the composite coating has a higher adhesion to the metal substrate than the pure epoxy coating. The reason is believed to be that the chemical bond formed by the N atoms and π electron groups on the aniline trimer by interaction with the carbon steel, caused the aniline trimer to be absorbed into the metal substrate [38]. When aniline trimer is in contact with the metal surface, nitrogen atoms, aryl groups and other groups containing lone electron and delocalized π electrons in their molecular structure will form a stable complex with iron atoms or ions through coordination bonds, improving the connection density between the coating and the metal substrate. Therefore, in the presence of a corrosive medium, aniline trimer modified GO can significantly limit the lamination and peeling of coatings.

4. Conclusion

In this work, an effective approach to improve the corrosion resistance of epoxy coating was demonstrated. ATGO composites were prepared by modifying GO with aniline trimer, and ATGO/EP composite coatings were prepared by adding amino modified GO to epoxy primer. The following conclusions were drawn from the research.

(1) The phase structure of ATGO prepared at different reaction temperatures was characterized by XRD, Raman spectra and FT-IR, and it was found that among the four reaction temperatures of 65 °C, 80 °C, 95 °C and 110 °C, aniline trimer has the best modification effect on GO at 95 °C.

(2) The surface morphology of the modified GO before and after the reaction was analyzed by AFM and TEM at 95 °C. It was confirmed that the modification treatment of GO by aniline trimer was successful, and that the layered structure of the original GO was not damaged after the modification.

(3) EIS, salt spray tests and adhesion tests were employed to analyze the influence of different addition amount of ATGO on the anticorrosion performance of composite coating. It was found that the coatings with ATGO added had significantly improved corrosion resistance, and among the three mass fractions of 0.05%, 0.1% and 0.3% of aniline trimer, the composite coating with 0.05% had the best corrosion resistance.
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References

[1] Milosev I 2019 Acta Chimica Slovaca 66 511–33
[2] Chhoaomousv V, Metner M and Boonyongmaneerat Y 2020 Journal of Coatings Technology and Research 17 583–95
[3] Furbuth W 2020 Materials 13 1–3
[4] Seidi F, Jouyandeh M, Taghizadeh M, Taghizadeh A, Vahabi H, Habibzadeh S, Formera K and Saeh M R 2020 Materials 13 1–16
[5] Kongparakul S, Kornprasert S, Suriyip L, De L, Sartam C, Chantarasisi N, Prasassarakih P and Guan G 2017 Progress in Organic Coatings 104 173–9
[6] McMahon M E, Santucci R J Jr, Glover C F, Kannan B, Walsh Z R and Scully J R 2019 Frontiers in Materials 6
[7] Wang C, Wang H, Li M, Liu Z, Lv C, Zhu Y and Bao N 2018 Journal of the Taiwan Institute of Chemical Engineers 85 248–56
[8] Radhamani A Y, Lau H C and Ramakrishna S 2020 Journal of Composite Materials 54 681–701
[9] Verma S, Mohanty S and Nayak S K 2019 Journal of Coatings Technology and Research 16 307–38
[10] Dutta D, Ganda A F, Chih J K, Huang C C, Tseng C J and Su C Y 2018 Nanoscale 10 12612–24
[11] Chen F G, Zhou D, Yang L P, Sun J T and Wu J 2019 Materials Research Express 6 1–10
[12] Ding R, Chen S, Lv J, Gui T J, Wang X, Zhao X D, Liu J, Li B J, Song Y L and Li W H 2019 Acta Chimica Sinica 77 1140–55
[13] Wei J, Thuc V and Inam F 2015 Rsc Advances 5 73510–24
[14] Um J G, Jun Y S, Elkamel A and Yu A 2020 Canadian Journal of Chemical Engineering 98 1084–96
[15] Jia S, Yao Z J, Zhang S S, Zhang Z L, Tao X W, Liu Y Y and Sun J C 2019 Materials Research Express 6 1–15
[16] Li J, Cui J, Yang J, Ma Y, Qiu H and Yang J 2016 Progress in Organic Coatings 99 443–51
[17] Othman N H, Ismail M C, Mustapha M, Salib N, Kex K E and Jiaal B A 2019 Progress in Organic Coatings 135 82–99
[18] Guo H, Zhang R, Zhao Z, Zou M, Chen X, He Z, Qu T, Li C and Huang G 2019 Technology 6 1–5
[19] Ghauri F A, Raza M A, Baig M S and Ibrahim M 2017 Materials Research Express 4 1–9
[20] Liu Y 3rd Int. Conf. on Energy Environment and Materials Science 942017
[21] Georgakilas V, Tiwari J N, Kemp K C, Perman J A, Bourlinos A B, Varelas N, Bafas V, Ichou F, Pham D H and Zboril R 2016 Chemical Reviews 116 5464–519
[22] Zhang C, Dai X, Wang Y, Sun Y, Li P, Qu L, Li X and Dou Y 2019 Coatings 9 1–15
[23] Domene-Lopez D, Sarabia-Riquelme R, Garcia-Quesada J C and Martin-Gullon I 2019 Coatings 9 1–15
[24] Zhang X, Yang X, Zhang M, Xu X, Sun G and You B 2019 Journal of Materials Science 54 3032–68
[25] Guo T, Li H, Ma X, Shi L, Wang W, Zhang W and Li L 2020 Plastics Rubber and Composites 49 245–53
[26] Shu S et al 2018 4th Int. Conf. on Applied Materials and Manufacturing Technology 423
[27] Ramezanzadeh B, Niroumandrad S, Ahmadi A, Mahdavian M and Moghadam M H M 2016 Corrosion Science 103 283–304
[28] Yu J, Zhao W, Liu G, Wu Y and Wang D 2018 Surface Topography–Metrology and Properties 6 1–12
[29] Xiong L, Yu M, Li Y, Kong X, Li S and Liu J 2020 Progress in Organic Coatings 142 1–11
[30] Paliapannan N, Cole A and Kuznetsov A E 2020 Rsc Advances 10 11426–34
[31] Lu H, Zhang Y T, Li W H, Cui Y A and Yang T 2017 Acs Applied Materials & Interfaces 9 4034–43
[32] Li J, Jiang Z, Gan L, Qiu H, Yang G and Yang J 2018 Composites Communications 9 6–10
[33] Yadav A, Kumar R and Sahoo P 2020 Acs Applied Nano Materials 3 3540–57
[34] Perez C, Leon I, Lesarri A, Pate B H, Martinez R, Millan J and Fernandez J A 2018 Angewandte Chemie-International Edition 57 15112–16
[35] Guo H, Yan J, Zhang R, He Z, Zhao Z, Qu T, Wan M, Liu J and Li C 2019 Advances in Materials Science and Engineering 2019 1–8
[36] Guo H, Chen M, Zhang R, Li J, Li C, Qu T, Huang G Q, He Z and Zeng Y 2019 Shock and Vibration 1–11
[37] Guo H F, Zhao Q, Nan D, Cai Y G and Yan J W 2020 Journal of the Brazilian Society of Mechanical Sciences and Engineering 42 1–9
[38] Ye Y W, Liu W, Liu Z Y, Zhang D W, Zhao H C, Wang L P and Li X G 2018 Journal of Sol-Gel Science and Technology 87 464–77