Computation of Binding Energy of MCS and GO-Grafted MCS with Waterborne Epoxy Resin Using Density Functional Theory Method: Investigating the Corrosion Resistance of the Composite Coatings

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ABSTRACT: In order to overcome the problems of poor corrosion resistance and low hydrophobicity of water-based coatings. Two corrosion-inhibiting materials, graphene oxide (GO) and modified chitosan (MCS), were added to the coatings to obtain a new type of coating with comprehensive properties. The composite material formed by PVA cross-linked waterborne epoxy resin was named "substrate". The density functional theory (DFT) calculation was used to explore the binding ability of MCS and GO-grafted MCS to the substrate, respectively. The results showed that the complex cross-linked network structure formed by the grafting of GO and MCS not only improved the intermolecular interaction force but also improved the binding ability to the substrate, and the coating is denser, effectively delaying the erosion to the coating by the corrosive medium. The composite coating exhibited excellent dual functional properties of hydrophobicity and corrosion resistance at the coating−metal interface, and a stronger protective effect was formed upon the steel plate. Studies showed that this composite coating has good hydrophobic properties. (The contact angle of the composite waterborne coating reaches 87°.) It also has low self-corrosion current (0.28/cm²−2) and high corrosion voltage (−0.45 V). The maximum inhibition efficiency of the coating is 99.97%.

1. INTRODUCTION

As a basic material for national infrastructure production, the service time of metal materials is limited due to the occurrence of corrosion. The hazards caused by corrosion have spread to almost all manufacturing industries, such as shortening the life of the project and even leading to major disasters.1−3 Forming a coating on the metal surface is an effective anticorrosion measure. Waterborne epoxy resin has broad application prospects and benefits, such as high protection efficiency and environmentally friendly compared with organic-solvent-based epoxy resin.4,5 However, a huge tension will be generated in the surface of the water-based paint in the application which caused shrinkage in the coatings.6,7 Although the doping of carbon nanotubes and titanium dioxide in the composite coating can improve the corrosion resistance of the coating, it will reduce the hydrophobicity of the coating. Furthermore, both materials tend to agglomerate in water-based epoxy resins, which limit their applications in composite coatings.8

Graphene oxide (GO) is a two-dimensional carbon nanomaterial with unique monatomic thickness, which can form a corrosion barrier in the coating and form a diffusion barrier to water and other corrosive media.9 Studies have also shown GO in the coating can slow down the corrosion of metal ions on the coating.10,11 The excellent chemical stability and electrochemical properties of GO greatly improve the stability of the coating.12 Based on this, GO has been widely used in the field of anticorrosion due to its excellent comprehensive properties, especially good water solubility and corrosion resistance. The combination with water-based epoxy resin also greatly improves the corrosion resistance of water-based coatings.13−15 In addition, chitosan (CS) is a natural polymer with good biocompatibility and excellent film-forming properties.16−19 Nevertheless, the regularity of chitosan molecules and intermolecular hydrogen bonds make it difficult to dissolve in most organic solvents and water, but it can be dissolved in some weak acids.20 The solubility of chitosan was improved by modifying chitosan with glacial acetic acid (the modified chitosan is named MCS).21 Furthermore, poly(vinyl alcohol) (PVA) is a nontoxic, harmless, and degradable polymer. Because of its good water
solubility and biocompatibility, it is often used as a curing agent to improve the flatness and smoothness of waterborne coatings.  

Through the investigation of a large number of literatures, it is found that few people have studied the binding energy between corrosion-inhibiting materials such as chitosan, graphene oxide, and epoxy resin. Therefore, only analyzing the corrosion resistance of the coating from the surface of the coating cannot really reflect the corrosion resistance of the coating. Our research team used density functional theory (DFT) calculation to explore the strength of the reaction between molecules in the coating and the magnitude of the binding energy between them, and then to study the corrosion resistance and hydrophobicity of the composite coatings.

In this paper, a water-based environmentally friendly composite coating with corrosion resistance and high hydrophobicity was prepared by compounding GO and MCS in water-based epoxy resin coatings. By grafting GO onto MCS, a cross-linked network structure is formed, and quantum theoretical calculations prove that this structure has a stronger binding energy to the substrate. The internal structure of the composite coating is more compact, which reduces the free energy of the coating surface and improves the hydrophobicity of the coating. The complex network structure formed also prevents corrosive media from penetrating the coating and eroding the substrate. Due to the excellent dispersibility and strong curing property of PVA in the coating, the composite coating has a good film-forming property, and the structure of the coating is more compact. Characterization methods such as electrochemical and contact angle tests show that our prepared coatings exhibit excellent corrosion resistance and high hydrophobic performance.

2. EXPERIMENTAL SECTION

2.1. Materials. GO was prepared by ourselves in our own laboratory with an improved Hummers method. The preparation method and physicochemical characterization of GO were shown in our published literature.  

CS (purity: 99%, viscosity: 400 mPa·s), PVA, natural granular graphite (purity 99%), potassium nitrate, concentrated sulfuric acid (98%), potassium permanganate, and chloride sodium were purchased from Shanghai Aladdin Company. The water-based epoxy resin (3EE101W) was purchased from Guangzhou Tongde Chemical Company, and glacial acetic acid was added to the solution until seeing that the viscous liquid stopped dripping. The modified chitosan (MCS) solution was obtained.

Next, 0.01 g of GO and 4 g of distilled water were put into a centrifuge tube and crushed in an ultrasonic crusher for 2 h. The broken GO solution and 0.4 g of MCS solution were put into a beaker, and the beaker was stirred on a constant temperature magnetic stirrer at 70 °C for 1 h. The GO-MCS solution was obtained.

2.3. Synthesis of P-E, P-EMC, and P-EMCG Waterborne Epoxy Resin Composite Coating. First, 3 g of water-based epoxy resin and 2 g of prepared PVA solution were measured (the concentration of the prepared PVA solution is 4%). After stirring at 70 °C for 40 min, the emulsion was evenly coated on Q235 steel plate (Q235 steel plate was from China Iron and Steel Research Institute). The size of steel is 10 mm × 10 mm × 1 mm, and the steel plate was polished with 400, 800, and 2000 mesh SiC sandpaper successively. Then the steel plate was placed in a JA-2000 ultrasonic oscillator containing acetone solution to be sonicated for 30 min. After removal from acetone solution, the surface of the steel plate was cleaned with ethanol, and finally dried at room temperature.)  

The coating prepared by the above method was named P-E.

For P-EMC, 0.4 g of MCS was added to the mixed solution which contains 3 g of water-based epoxy resin and 2 g of PVA. After ultrasonic shock for 30 min, mechanical stirring was performed at 70 °C for 1 h. The coating on the steel plate was named P-EMC. According to the mass ratio of GO to distilled water of 1:1000, 5 g of mixed solution were weighed and ultrasonically broken for 1 h, and the GO emulsion was obtained. The emulsion was added to the prepared P-EMC solution under the same preparation conditions, and the coating was named P-EMCG. The newly prepared coating was dried in a vacuum-drying oven at 50 °C for 1 h. The thickness of each composite coating is 60 ± 5 μm.

2.4. Characterization. The D8-DISCOVER X-ray diffractometer produced in Germany is used to analyze the uniformity of the surface dispersion of the three coatings, and the diffraction angle range is 5°–40°. The contact angles of the liquid to the coatings and the hydrophobicity of the coatings were measured by the contact angle meter (CA100A). A Nicolet AVATAR-330 FTIR spectrometer (collection range is 1000–4000 cm⁻¹) and an X-ray photoelectron spectrometer (XPS) were used to verify the successful cross-linking of MCS and GO in the coating. Field-emission electron microscopy (ZEISS-6035) was used to test the corrosion resistance of the three coatings. The polarization curves and electrochemical impedance spectra (EIS) of the uncorroded coating and the coating soaked in 4% NaCl solution for 20 days were tested. Both test methods were tested in a three-electrode system. The reference electrode is a calomel electrode, the counter electrode is a platinum electrode. The working electrode is a steel plate with a coating area of 1 cm². The frequency range of EIS test is from 1 × 10⁵ to 1 × 10⁻² Hz.

2.5. Details of Quantum Mechanics Modeling. DFT calculations were used to better explore the strength of the binding ability of MCS and GO-grafted MCS to the substrate and then compare the corrosion resistance of the two composite coatings. The geometries were subjected to optimization carried out using the DFT method with M06-2X functional in conjunction with 6-31G(d,p) basis set. The calculated temperature is 70 °C. All QM computations were done using program Gaussian 16, and DFT-D3 dispersion correction was added. In order to make the binding energy more accurate, we corrected the basis set superposition errors (BSSE). The BSSE was calculated using the counterpoise method developed by Boys and Bernardi in the Gaussian program.
3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The Fourier transform infrared spectra of CS, MCS, and GO-MCS are shown in Figure 1a. The existence of $\text{OH}$, $\text{N-H}$, and $\text{C=O}$ groups was confirmed by infrared spectroscopy. The stretching vibration peak of $\text{OH}$ group appeared at 3423 cm$^{-1}$. Compared with CS, the $\text{OH}$ group of MCS is not significantly reduced on the $\text{OH}$ characteristic peak. This is because the modification of chitosan by glacial acetic acid mainly consumes the intermolecular hydrogen bonds of chitosan. The GO-modified CS consumes the polar hydrophilic group $\text{OH}$ again, providing a theoretical basis for the contact angle experiments. The characteristic waves of $\text{CH}$ and $\text{N-H}$ at 2924 and 1650 cm$^{-1}$ did not fluctuate significantly, indicating that the structure of MCS did not change. $\text{C=O}$ stretching vibration peak appeared at 1602 cm$^{-1}$, which was caused by the $\text{C=O}$ double bond in GO, indicating that GO was successfully combined into the coating. The addition of GO not only improves the intermolecular binding force but also improves the curing and cross-linking reaction of the coatings. The infrared spectrum of the synthesized composite coating materials of P-E, P-EMC, and P-EMCG coatings are presented in Figure 1b. For the P-E sample, due to the large number of intermolecular hydrogen bonds, the stretching vibration of $\text{OH}$ group is quite intense. For P-EMC coating, the peaks at 3425 and 1602 cm$^{-1}$ are obtained from the stretching vibrations of the $\text{OH}$ and $\text{N-H}$ groups. For P-EMCG coating, the peaks at 3423, 1734, 1607, and 1296 cm$^{-1}$ are obtained from the stretching vibrations of the $\text{OH}$, $\text{CH}$, $\text{C=O}$ and $\text{C-N}$ groups, respectively. It can be seen from the figure that the $\text{OH}$ and $\text{N-H}$ stretching vibration frequency has a slight deviation, indicating that the
strength of the key has changed. It is demonstrated that bond breaks and reorganizations occurred between molecules. Compared with P-EMC, the −OH stretching vibration band of P-EMCG has narrowed, which demonstrates that there is a certain degree of consumption of intramolecular hydrogen bonds, confirming that GO was successfully grafted onto MCS. The C=O peak which appeared at 1734 cm$^{-1}$ indicates that GO and P-EMC were successfully cross-linked. The peak at 1296 cm$^{-1}$ is caused by the stretching and vibration of C−N. Comparing the two coatings, the peak at 1296 cm$^{-1}$ shows a wavenumber shift and the C−N bond energy changes. This may be due to the C−N bond breaking and recombination. It is also proved that GO and MCS have cross-linked and compounded.

Figure 1c displayed the Raman spectrum of GO-MCS and GO. It can be seen from the figure that GO has two peaks at 1360 and 1590 cm$^{-1}$, namely, the D and G peaks. The D peak represents the defect of the carbon atom lattice in GO, and the G peak represents the stretching vibration in the sp$^2$ plane of the C atom. GO-MCS has a slight Raman shift relative to GO, indicating that a new chemical bond is formed between MCS and GO. In addition, the ratio of $I_D/I_G$ represents the defect degree of GO. The value of $I_D/I_G$ decreases from 0.939 to 0.916 illustrate that the grafting of GO and MCS reduces the defects of the coating.40−42

The XRD diffraction peaks of P-E, P-EMC, and P-EMCG coatings are shown in Figure 1d. XRD patterns of MCS and GO-MCS composites are displayed in Figure 1d1. The graphene oxide (GO), which was prepared by us was performed by X-ray diffraction and TEM (Figure 1e,f). The SEM analysis on the cross section of the P-EMCG coating is also shown in Figure 1g.

Figure 2. Diagram of sedimentation test of CS and MCS (a−c), diagram of sedimentation test of GO and GO-MCS (a1, b1, and c1), cross-linking principle of GO and MCS (d).
It can be seen from Figure 1e that strong diffraction peaks appear at 13.4 and 26.3°, corresponding to the characteristic peaks of GO and graphite on the (002) crystal plane, respectively. The interlayer spacings of GO and graphite were calculated to be 0.68 and 0.35 nm by the Bragg equation. As shown in Figure 1e, the diffraction peak at 17.5° in the P-EMCG coating is still the characteristic peak of GO. Compared with GO, the diffraction peaks appear to be significantly shifted to the right, and the intensity is reduced, indicating that the interlayer spacing of GO is reduced, which can be attributed to the introduction of more functional groups formed by grafting around the GO lamellae through bonding inside the coating, leading to the decrease of the layer spacing of GO from 0.68 to 0.51 nm. The diffraction peak appearing at 21.5° is the diffraction peak of a small amount of graphite present in the GO, and the diffraction peak almost disappeared. This showed that the purity of GO prepared by us was relatively high. Another reason is that when GO was added to the coating, the interlayer spacing of graphite itself is smaller than that of GO. The residual graphite is small and uniformly dispersed in the coating, so the intensity of the diffraction peaks is weak. In addition, the peaks of P-EMCG are sharper than those of the other two coatings, indicating the higher crystallinity of the P-EMCG coatings. With the increase of crystallinity, the coating exhibits more excellent tensile strength and high temperature thermal stability.  

As shown in Figure 1f, the TEM image of GO exhibits an obvious transparent layered structure. In order to explore the internal morphology of the P-EMCG coating, the SEM analysis on the cross section of the P-EMCG coating was performed. We can see from the Figure 1g that there is an ordered layered structure inside the coating, and the interlayer spacing between the layers is basically the same, which is basically consistent with the above XRD analysis. Figure 2a is a graph of the sedimentation test of MCS, CS, GO, and GO-MCS. It can be seen from the figure that unmodified chitosan and GO have poor water solubility. It is difficult to disperse uniformly in water to form a suspension, and obvious stratification occurs. CS is almost completely precipitated after 5 days. MCS can be uniformly dispersed in the solution and still presents a colloidal system for a long time. After GO was grafted onto MCS, the dispersibility of both was greatly improved. It shows that GO was successfully grafted onto MCS. The regularity of chitosan molecules and intermolecular hydrogen bonds make it difficult to dissolve in most organic solvents and water, but it can be dissolved in some weak acids. H+ in glacial acetic acid can protonate the –NH2 of chitosan into –NH3+, and the hydrogen bond in chitosan is destroyed, which also explains the reason why chitosan is soluble in acid but cannot be dissolved in water. Therefore, although the electrophilic property of the –NH2 is stronger than that of the –OH, the binding strength of the –NH2 is also decreased because part of the amino group of the chitosan has been destroyed by glacial acetic acid, and the number of –NH2 in a chitosan is less than that of the –OH. Furthermore, it proves the successful construction of the whole experimental system. The cross-linking principle of MCS between GO is shown in Figure 2d. The carboxyl groups of GO are grafted with amino groups and hydroxyl groups of MCS to form complex
macromolecular network structures. DFT calculations prove that this structure has a larger binding energy to the substrate, and the strong binding force formed inside the coating prevents NaCl molecules from corroding into the coating. The corrosion path expansion in the coating was delayed, thereby improving the corrosion resistance of the coating.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical structures of P-EMC and P-EMCG. From the XPS total spectrum (Figure 3a), P-E, P-EMC, and P-EMCG have O 1s and C 1s peaks at 532.5 and 285.4 eV. Compared with P-EMC, P-EMCG has a smaller N 1s peak at 399.0 eV, and a N 1s peak was not detected in P-E. The N 1s peak in P-EMC indicates that MCS has been successfully incorporated into the coating. The N1 peak in P-EMCG is smaller than that of P-EMC, which is due to the consumption of $-\text{NH}_2$ in MCS during the grafting of GO with MCS. The strong cross-linking reaction makes the amino group difficult to be observed in the XPS total spectrum (Figure 3a). Two peaks of 286.4 and 284.6 eV can be found from the C 1s spectrum of P-EMC coating, corresponding to C–O and C–C bond (Figure 3b). However, the C 1s spectrum of P-EMCG was fit to three peak positions with binding energies of 286.5 eV (C–O), 284.9 eV (C–C), and 288.7 eV (O–C=O) (Figure 3c). The emergence of new O–C=O confirmed the successful composite of GO with the P-EMC coating.

Figure 4. Binding energy of MCS and substrate at different sites. The unit of binding energy is kcal/mol, and the unit of bond length is Å.

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3d demonstrates the presence of N–H (400.5 eV) and C–N (399.5 eV) in P-EMCG coating.

3.2. Quantum Mechanics Calculations. The binding energy of MCS and substrate at different sites are presented in Figure 4. The binding energy between each site can be calculated with the formula \( \Delta E_{\text{binding}} = E_{\text{MCS/substrate}} - (E_{\text{MCS}} + E_{\text{substrate}}) \). \( E_{\text{MCS/substrate}} \) represents the electronic energy optimized by the combination of MCS and the substrate, \( E_{\text{MCS}} \) represents the electronic energy optimized by chitosan, and \( E_{\text{substrate}} \) represents the electronic energy optimized by the substrate. Nine different sites were selected to calculate. The initial conformation, final conformation, and binding energy are shown in Figure 4. The unit of binding energy is kcal/mol, and the unit of bond length is Å. (The calculation results are respectively expressed as MCS-S-1, MCS-S-2, MCS-S-3, MCS-S-4, MCS-S-5, MCS-S-6, MCS-S-7, MCS-S-8, and MCS-S-9). The corrected binding energy was calculated according to eq 1, and eq 2 is the conversion method of “a.u.” and “kcal/mol”.

\[
\Delta E_{\text{binding-correct}} = \Delta E_{\text{binding}} + \text{BSSE} \tag{1}
\]

\[
\text{kcal/mol} = \text{a.u.} \times 627.5029 \tag{2}
\]

As Table 1 presents, the binding energy of MCS to the substrate is low, and the average binding energy is only -11.28075 kcal/mol. The reason for this is that the chitosan has fewer cross-linking sites with the substrate, and the binding force is weak, indicating chitosan has low binding ability with waterborne epoxy resin and PVA. Therefore, this causes the P-EMCG coating to be brittle and easy to fall off. This situation verifies the poor performance of the P-EMC coating in the actual picture in Figure 9b.

The binding energy of GO-MCS and substrate was also calculated. \( E_{\text{GO-MCS/substrate}} \) represents the optimized electronic energy of GO grafted MCS with the substrate, \( E_{\text{GO-MCS}} \) represents the optimized electronic energy of GO grafted MCS, and \( E_{\text{substrate}} \) represents the optimized electronic energy of the substrate of electronic energy. Six different sites were calculated. The initial conformation, final conformation and binding energy are shown in Figure 5. (The calculation results are respectively expressed as GO-MCS-substrate-1, GO-MCS-S-2, GO-MCS-S-3, GO-MCS-S-4, GO-MCS-S-5, and GO-MCS-S-6.) The complex network structure formed after GO and MCS grafted in the coating can not only hinder the damage of the corrosive medium to the coating, but also form more cross-linking sites after the combination. According to the eqs 1 and 2, The BSSE and corrected binding energy of GO-MCS-Substrate are shown in Table 2. Different sites to bind to the substrate sites were selected, the average binding energy reached -28.67850 kcal/mol. Compared with the MCS-substrate structure, GO-MCS structure exhibited a stronger binding ability to the substrate than a single MCS, which means that the GO-MCS-substrate structure has better stability to prevent corrosion medium through the coating on the erosion of the steel.

### Table 1. BSSE and Corrected Binding Energy of MCS–Substrate

|   | \( E \) (hartree) | \( \Delta E_{\text{binding}} \) (hartree) | \( \Delta E_{\text{binding}} \) (kcal/mol) | BSSE (a.u.) | \( \Delta E_{\text{binding-correct}} \) (kcal/mol) |
|---|------------------|-----------------|----------------|------------|-------------------------------|
|  |                 |                 |                |            |                               |
| MCS-S-1 | -2725.701874 | -0.037271 | 23.876605 | 0.01225517 | -15.69750 |
| MCS-S-2 | -2725.698876 | -0.034273 | 21.5064068 | 0.012850633 | -13.44260 |
| MCS-S-3 | -2725.683031 | -0.018428 | 11.5636234 | 0.007910906 | -6.59951 |
| MCS-S-4 | -2725.693157 | -0.028554 | 17.9171718 | 0.010407245 | -11.38714 |
| MCS-S-5 | -2725.679601 | -0.014998 | -9.41128449 | 0.007534661 | -4.68327 |
| MCS-S-6 | -2725.683834 | -0.023751 | 14.9038213 | 0.007573624 | -5.73059 |
| MCS-S-7 | -2725.681309 | -0.016706 | 10.4830634 | 0.010573298 | -3.69305 |
| MCS-S-8 | -2725.696437 | -0.031384 | 19.9759273 | 0.010683387 | -13.27207 |
| MCS-S-9 | -2725.717756 | -0.053153 | 33.3536616 | 0.020102075 | -20.73955 |

3.3. Coating Performance. 3.3.1. EIS Measurements. Electrochemical impedance (EIS) was used to analyze the corrosion resistance of the three coatings of P-E, P-EMC, and P-EMCG before corrosion and after immersion in 4% NaCl solution for 20 days. Figure 6 shows the Bode and Nyquist plots of the coatings. The coating has a higher impedance modulus and impedance arc radius before immersion, and exhibits higher corrosion resistance (Figure 6a). As the immersion time in NaCl solution increases, the corrosion effect gradually deepens and penetrates into the coating. The impedance arc is significantly reduced (Figure 6b). However, the impedance modulus and impedance arc radius of P-EMCG coating are always higher than P-E and P-EMC coating.

As shown in (Figure 6a1,b1), as the immersion time increases, \( |Z|_{\text{b,01 Hz}} \) decreases. Due to the low cross-linking density of P-E coatings, there is no barrier to the corrosive medium by the cross-linked structure. The NaCl solution can easily penetrate into the coating, and the structure of the coating was destroyed. The addition of GO and MCS formed an intricate cross-linked structure inside the molecule. The calculations prove that this structure has a larger binding energy to the substrate, and the stronger binding force formed inside the coating prevents NaCl molecules from corroding into the coating. Besides, the hydrophilic functional groups of the molecules were reduced after the GO was grafted onto MCS, and the hydrophilicity of the coating was reduced, which to a certain extent provides a barrier for the penetration of water molecules into the coating. Thus, P-EMCG has a higher dielectric constant, and the corrosion resistance was also greatly improved.

The equivalent circuit diagram of the simulation of the EIS result is presented in Figure 6c,d. \( R_s \) is the solution resistance, \( R_C \) is the coating resistance, \( R_{ct} \) is the charge transfer resistance, \( C_p \) is the coating capacitance, and \( C_{dl} \) represents the double-layer capacitance of the steel surface. Figure 6c,d shows the equivalent circuit diagram of the coatings during the early and late corrosion of NaCl solution. Figure 6c is an equivalent circuit diagram of the corrosive medium not penetrating to the surface of the Q235 steel, and Figure 6d is an equivalent circuit diagram of the corrosive medium passing through the coating to corrode the surface of the Q235 steel. In the initial stage, the coating has good protective properties, and in the later stage, the corrosive medium reaches the steel surface through the coating gap. The resistance (\( R_{ct} \)), which represents the...
performance of the coating, is connected in series with the electric double-layer circuit, which represents the electrochemical signature of metal corrosion. It shows that the protection ability of the coating to the substrate decreases in the later stage of corrosion.

### 3.3.2. Potentiodynamic Polarization Curve and Tafel Test

Figure 7 shows the polarization curves of P-E, P-EMC, and P-EMCG coatings before and after corrosion, which was to further explore the corrosion resistance of the coatings. The corrosion resistance of the coating is reflected in the corrosion potential ($E_{\text{corr}}$) and corrosion current density ($I_{\text{corr}}$) of the polarization curve. The corrosion resistance is inversely proportional to the corrosion potential and the corrosion current density. It can be seen from Figure 8 that P-EMCG has the lowest $E_{\text{corr}}$ and $I_{\text{corr}}$, indicating that P-EMCG has the lowest electrical conductivity. The complex network structure formed by MCS and GO reduces the electrical conductivity of the coating, and the corrosion resistance of the coating was greatly improved. The $E_{\text{corr}}$ and $I_{\text{corr}}$ of the coatings after corrosion were reduced correspondingly. This is because the structure of the coating was destroyed by the electrolyte solution, and the corrosion resistance was also correspondingly reduced.

In order to more intuitively reflect the corrosion resistance of the three coatings, the $E_{\text{corr}}$ and $I_{\text{corr}}$ of the Tafel diagram are fitted. The polarization resistance ($R_p$) of the coating was calculated using the Stern–Geary equation (eq 3). The protection efficiency ($P_E$) was calculated through eq 4,

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

The $P_E$ of the coating was calculated using eq 4, and the calculated results are shown in Table 1.

$$P_E = \frac{I_{\text{corr}}(\text{uncoated}) \times I_{\text{corr}}(\text{coated})}{I_{\text{corr}}(\text{uncoated})} \times 100\%$$

We can see from Table 3 that the $R_p$ value of P-EMCG is the largest, far exceeding the values of P-E and P-EMC. The $P_E$ of P-E and P-EMC were 96.93 and 98.19%, respectively, while the $P_E$ of P-EMCG reached 99.97%. Both the polarization curve and the Tafel test show that P-EMCG has high corrosion resistance.

### 3.4. Characterization of Corrosion Products on Coating Surface and Protection Mechanism of Coating

Figure 8 is the SEM images of the three coatings before corrosion and after immersion in 4% NaCl solution for 20 days. The surface of the coating was smooth before corroded, only slight agglomeration appeared on the P-E coating. After corrosion, a large number of NaCl molecules are attached to the surface of the P-E coating (Figure 8a1). There are cracks and peeling on the surface. A large number of corrosion pits appear on the surface of the coating. The NaCl completely destroys the structure of the coating and corrodes to the surface of the steel plate. The corrosion pits on the surface of the P-EMC coating were significantly reduced (Figure 8b1). NaCl adheres to the surface, which only damages the surface of the coating. It does not completely corrode to the inside of the coating, indicating that MCS hinders the intrusion of NaCl molecules. Compared with the P-E and P-EMC coatings, P-EMCG coating did not appear a large number of corrosion pits, and there is no agglomeration on the surface of the coating.
coating, which still maintains the morphology before corrosion (Figure 8c1). The reason is that the complex structure formed by GO and MCS enhances the bonding force inside the coating and the adhesion to the substrate, which blocks the erosion of the coating by the corrosive medium.

In order to verify the hydrophobic properties of the coating, a contact angle experiment was carried out. As shown in Figure 8, the contact angle of the P-E coating is only 47°. This is because PVA has a large number of −OH groups, and −OH is a hydrophilic group, so the coating has poor hydrophobicity. The contact angle of the P-EMC coating is further increased (Figure 8b). The modification of CS with glacial acetic acid eliminates the intermolecular hydrogen bond and also consumes the −OH groups of PVA and CS. The regularity of chitosan molecules and intermolecular hydrogen bonds make it difficult to dissolve in most organic solvents and water, but it can be dissolved in some weak acids. H⁺ in glacial acetic acid can protonate the −NH₂ of chitosan into −NH₃⁺. In addition, glacial acetic acid can be esterified with CS and PVA, that is, the −COOH of glacial acetic acid is esterified with −OH of CS and PVA. The polar groups of amino and hydroxyl groups in CS and the hydroxyl groups of PVA are destroyed. Thus, the intermolecular hydrogen bonds of MCS are destroyed. Therefore, the hydrophobic performance of the coating will be improved compared with the P-E coating. The contact angle of P-EMCG coating reaches 87° (Figure 8c) and has excellent hydrophobic properties. The grafting of GO and MCS not only makes the inner structure of the coating denser but also reduces the value of the surface free energy, and the hydrophobic properties of the coating were improved.

Table 2. BSSE and Corrected Binding Energy of GO-MCS-Substrate

| GO-MCS-S | E (hartree) | ΔEbinding (hartree) | ΔEbinding(kcal/mol) | BSSE (a.u.) | ΔEbinding-correct(kcal/mol) |
|----------|-------------|---------------------|---------------------|-------------|-----------------------------|
| GO-MCS-S-1 | −7010.973765 | −0.075178 | −47.17441302 | 0.031889179 | −27.16386 |
| GO-MCS-S-2 | −7010.955654 | −0.057067 | −35.80970799 | 0.023972836 | −20.76668 |
| GO-MCS-S-3 | −7010.987597 | −0.08901 | −55.85403313 | 0.034759208 | −34.04253 |
| GO-MCS-S-4 | −7010.982377 | −0.08379 | −52.57846799 | 0.03381134 | −31.36175 |
| GO-MCS-S-5 | −7010.971288 | −0.072701 | −45.62008833 | 0.024956415 | −29.95987 |
| GO-MCS-S-6 | −7010.965326 | −0.066739 | −41.87891604 | 0.020880596 | −28.77628 |

Figure 6. Nyquist and Bode of three coatings uncorroded (a, a1) and immersed in 4% NaCl solution for 20 days (b, b1). Equivalent circuit for numerical simulation of the EIS measurements (c, d).

Figure 7. Polarization curves of bare steel, P-E, P-EMC, and P-EMCG coatings uncorroded (a) and immersed in 4% NaCl solution for 20 days (b).
The schematic illustration of corrosion protection mechanism for coatings is displayed in Figure 9a. Since the poor structural bonding and compactness inside the coating, the corrosive medium can easily diffuse into the interior of the coating. As the corrosion time increases, the corrosion path becomes wider and denser until the corrosion medium reaches the steel plate through the coating. Quantum mechanical calculations demonstrate that the binding energy of the P-EMC coating is weaker than that of P-EMCG (relevant calculations are given in section 3.2). Moreover, the chitosan molecules will agglomerate inside the coating, and the corrosion resistance of the coating is not significantly improved. GO-grafted MCS can not only improve its dispersibility but also greatly improve the binding energy of the formed cross-linked structure and the coating, delaying the erosion of the coating by the corrosive medium. It also inhibits the damage to the pores by the corrosive medium and preserves the original structure of the coating.

Figure 9b is the physical image of the corrosion resistance test of the three coatings under the standards of the Ministry of Aerospace Industry of the People’s Republic of China. After a lot of experiments, the test results meet the standards of the Ministry of Aerospace Industry and have excellent corrosion resistance. Direct titration method was used to verify the corrosion resistance of the composite coatings. The three prepared coatings were placed flat on the test table, and a small amount of concentrated nitric acid was taken up with a rubber dropper, and two drops were titrated on the surface of the coatings. After standing at room temperature for 15 s and 14 h, the corrosion resistance of the three coatings was compared by observing their surface morphology after corrosion. The whole operation process is carried out in the fume hood. This is an innovative idea from our team to test the corrosion resistance of three coatings in this way, which can directly and clearly observe the corrosion resistance of the coatings. Simultaneously, a concentrated nitric acid solution of 12 mol/L was titrated on the surface of the coating, and the surface morphology of the coating after 15 s and 14 h of corrosion was observed. It can be seen from the figure that the P-E and P-EMC coatings have turned yellow after 15 s of corrosion, and the P-EMCG coating has not changed significantly. After 14 h of corrosion, the P-E coating surface was completely corroded, and a lot of peeling and peeling phenomenon were observed. P-EMC coating was also corroded severely, and the structure of the coating was destroyed. Compared with the other two coatings, the structure of the P-EMCG coating was

Table 3. Electrochemical Corrosion Measurements of P-E, P-EMC, and P-EMCG Coatings

|          | working electrode | \( E_{corr} \) (V vs. SCE) | \( I_{corr} \) (μA/cm\(^2\)) | \( R_p \) (kΩ/cm\(^2\)) | \( P_E \) (%) |
|----------|-------------------|-----------------------------|-----------------------------|---------------------------|-------------|
| bare steel | −0.82 | 1322.16 | 1.6 | | |
| P-E | −0.54 | 40.58 | 30.1 | 96.93 | |
| P-EMC | −0.47 | 23.99 | 110.6 | 98.19 | |
| P-EMCG | −0.45 | 0.28 | 864.8 | 99.97 | |

Figure 9. Schematic illustration of corrosion protection mechanism for coatings (a). Physical drawings of P-E, P-EMC, and P-EMCG coatings uncorroded and after corrosion for 15 s and 14 h (b).
not damaged, and only slight peeling occurred on the surface which indicates that P-EMCG coating has excellent corrosion resistance.

4. CONCLUSIONS

The above studies showed that an environmentally friendly coating with corrosion resistance and high hydrophobicity was developed by combining inorganic and organic materials. The grafting of GO and MCS forms an intricate cross-linked structure, which forms a natural barrier in the coatings to block the corrosion of steel by corrosive media passing through the coating, and the coating has excellent corrosion resistance. Experiments showed that compared with P-E and P-EMC coatings, P-EMCG coatings have good corrosion resistance in both acidic and alkaline media. The grafting of GO and MCS consumes the polar hydrophilic groups in the molecules and reduces the value of the surface free energy, so the hydrophobic properties of the coating was further improved. Density functional theory (DFT) calculations have proved that the complex cross-linked structure formed by the grafting of graphene oxide and MCS not only improved the intermolecular interaction force but also enhanced the binding energy with water-based coatings, which makes the structure inside the coating more compact and effectively reduces the corrosion ability of the corrosive medium into the coating.

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Notes

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