Study on properties of porous SiO2/ GO modified polyurethane coatings loaded with corrosion inhibitor

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Abstract. Polyurethane (PU) coating can provide physical barrier for metal surface, but the penetration of corrosive ions will affect the long-term corrosion resistance of the coating. In order to improve the corrosion resistance of the coating, it is necessary to modify the coating to reduce the internal defects of the coating and improve the corrosion resistance of the coating. Using mesoporous silica (SiO2) as the carrier to support the corrosion inhibitor 2-mercaptobenzimidazole (MBI), and using the silane coupling agent GPTS as the bridging agent to compound with graphene oxide (GO) to prepare f-GO-MBI @SiO2 composite nano-materials, f-GO-MBI @SiO2 composite nano-materials are added to the polyurethane varnish in different proportions, and the f-GO-MBI @SiO2 modified PU coating is obtained on the surface of carbon steel by spraying method to improve the carbon corrosion resistance of steel substrate. The composition and loading conditions of drug-loaded composite nanomaterials were characterized by fourier infrared spectroscopy (FTIR) and laser particle size analyzer; electrochemical impedance spectroscopy (EIS) and neutral salt spray test were used to study the properties of different coatings corrosion resistance. The results shows that the addition of f-GO-MBI @SiO2 composite nano-materials significantly improves the corrosion resistance of the coating, the low addition amount will reduce the anti-corrosion effect, and the addition of too high can easily lead to agglomeration of composite nano-materials and produce paint film defects. When the addition amount of f-GO-MBI @SiO2 is 5 wt%, the low-frequency impedance of the coating is two orders of magnitude higher than that of the pure polyurethane coating, the corrosion spread width at the neutral salt spray scratches is reduced to 1.5 mm, and the coating has the best corrosion resistance.

1. Introduction
Polyurethane coating as a kind of important type anticorrosive coating is widely used in carbon steel corrosion protection areas, however, due to the invasion of O2, corrosive chloride ions easily form diffusion channels in the coating, resulting in slow infiltration of corrosive ions into the coating/steel interface, the coating corrosion resistance is reduced, lose the effect on the corrosion protection of the base material [1,2]. And the coating will fall off or crack due to the action of external forces, so that the surface of the substrate can not be effectively protected. In recent years, researchers usually improve the active anticorrosion performance of coatings by adding corrosion inhibitor. However, direct addition of corrosion inhibitor may interact with other components in coatings or cause corrosion inhibitor inactivation. Encapsulation of corrosion inhibitor in micro/nano containers can prevent its direct contact with coatings and overcome the disadvantages of direct doping [2].

Mesoporous SiO2 can effectively load corrosion inhibitors due to its uniform mesoporous structure, and enhance the adherence and flexibility of PU, but mesoporous SiO2 is easy to agglutinate, difficult to
disperse evenly in the organic system, affecting the anticorrosion effect [3,4]. Graphene oxide (GO), as a derivative of graphene, has a large specific surface area and excellent permeability resistance, which can effectively stop the corrosive medium, and its surface with a large amount of active oxygen containing functional groups, such as epoxy groups and hydroxyl, carboxyl, these functional groups sensitive to polar solvent added to GO easy dispersion, and makes the graphene oxide layer of negatively charged. It is beneficial to the loading of inorganic nanoparticles on go surface [5]. The composite of mesoporous silica and graphene oxide loaded with corrosion inhibitor and applied to PU coating can not only realize the loading and release of corrosion inhibitor, but also reduce the agglomeration of mesoporous SiO2 [6]. Moreover, the barrier property and corrosion resistance of PU coating can be further improved. In this paper, 2-mercaptobenzimidazole (MBI) was selected as corrosion inhibitor and loaded with mesoporous SiO2. The surface of GO was functionalized by GPTS (propyl trimethoxysilane). f-GO-MBI@SiO2 composite nanomaterials were prepared by bridging the silane coupling agent and doped into polyurethane varnish in different proportions. The corrosion resistance of composite coating was studied.

2. Experimental

2.1 Materials and Instruments

Q245 Sandblasting low carbon steel plate (150 mm ×70 mm × 3 mm), mesoporous SiO2 nanoparticles were purchased from Xiaofeng Nanomaterials Technology Co., LTD., 2-lucid benzimidazole (MBI), propyl trimethoxysilane (GPTS), ethanol, N,N dimethyl acetamide (DMA) are analytical pure, purchased from Sinopharm Chemical Reagent Co., LTD. Polyurethane varnish, commercially available. Spectrum Two Fourier Infrared Spectrometer (FTIR), Winner2308B Dry-wet Integrated Laser Particle Size analyzer, German EPK Minitest600BF Coating thickness tester, JYWX-010 Alternating salt spray test chamber, Gamry Electrochemical Workstation.

2.2 Preparation of drug-loaded nanocomposites

0.1g SiO2 was added to 10mL saturated 2-lucid benzimidazole (MBI) ethanol solution, stirred under vacuum conditions for 1h, centrifuged to obtain silica nanovessel loaded with MBI (MBI@SiO2), vacuum drying at 60℃ for 12h.

0.1 g of GO and 2 g of GPTS(propyl trimethoxysilane) were added to 90 g of anhydrous ethanol, and dispersed by ultrasonic to form a uniform solution. Stirred at 78℃ for 5h, 8g of distilled water was added slowly. After centrifugation and drying at 60℃ for 24 h, functionalized GO (f-GO) was obtained. 250 mg f-GO was added into 100 mL DMF solution, and ultrasonic dispersion was performed for 0.5 h to form a uniform suspension. Then, 50 mg MBI@SiO2 was added to the suspension for ultrasonic dispersion for 0.5 h. Finally, the mixture was stirred at 105℃ for 6 h, centrifuged, washed with ethanol and distilled water and dried in 60℃ oven for 24 h to obtain f-GO-MBI@SiO2 complex.

2.3 Preparation of polyurethane composite coating

Polyurethane composite coatings containing different proportions of f-GO-MBI@ SiO2 hybrid nanofillers were prepared by the following steps. First of all, the surface of the base material (Q245) is pretreated, and clean with ethanol, use after thoroughly drying. Secondly, the blending ratio of polyurethane varnish and curing agent is 2:1, and the prepared f-GO-MBI@ SiO2 hybrid nano-filler is added according to the mass ratio of 2 wt%, 5 wt% and 8 wt%. The components are fully mixed by ultrasonic shock and mechanical agitation to form uniform polyurethane composite coating, which is sprayed on the surface of the prepared steel plate. The coating thickness was controlled at 100 μm±10 μm, and the coating was cured at 65℃.

2.4 Testing and characterization

Spectrum Two infrared spectrometer (FT-IR) was used to analyze the molecular structures of GO, f-GO,
SiO₂, MBI@SiO₂ and f-GO-MBI@SiO₂ hybrid compounds. The particle size of mesoporous SiO₂ and MBI@SiO₂ nanoparticles was analyzed by Winner2308B laser particle size analyzer.

Test the adhesion of paint film according to GB/T 5210-2006 “Adhesion test of paint and varnish pulling method”. Impedance spectrum and Tafel test were carried out at 25°C by electrochemical workstation. The reference electrode was silver-Silver chloride electrode, the auxiliary electrode was Pt electrode, and the working electrode was a three-electrode system. The mass fraction of electrolyte solution was 3.5% NaCl solution. The scanning speed of 5mV/s was selected for the electrochemical polarization curve. According to GB/T 1771-2007 “Paint and Varnish resistance to neutral salt spray performance determination” test the corrosion resistance of the paint film, measure the degree of corrosion of the paint film by observing the width of the corrosion spread at the scratch.

3. Results and Discussion

3.1 Infrared spectrum (FT-IR) characterization

The composite between functionalized GO and MBI loaded mesoporous silica was studied by FT-IR. Figure 1 shows the infrared spectra of the synthesized GO, f-GO, SiO₂, MBI@SiO₂ and f-GO-MBI@SiO₂ composites. Figure 1 is the FT-IR spectrum of GO, according to Yu[5], the stretching vibration absorption peaks at 2934 cm⁻¹ and 2845 cm⁻¹ are -CH, and the absorption peak at 1226 cm⁻¹ represents C-O-C bonds. Figure1(b) corresponds to the infrared spectrum of f-GO, compared with GO, the characteristic peak of Si-O-Si appears at 1102 cm⁻¹ and the characteristic peak of Si-O-C appears at 1040 cm⁻¹, indicating that GO is successfully retouched by GPTS. Figure 1 (c) and (d) respectively correspond to pure SiO₂ and MBI@ SiO₂, according to Rong [7], in (d) there is an absorption peak at 1479 cm⁻¹ caused by the surface bending vibration of the C-H, and an absorption peak at 1649 cm⁻¹ caused by the vibration of the benzene ring skeleton, which indicates that the corrosion inhibitor MBI has been successfully doped into the composite coating. In addition, the existence of characteristic absorption peaks of Si-O-C and benzene ring skeleton in curve (e) indicates that mesoporous SiO₂ nanoparticles loaded with corrosion inhibitors have been successfully combined with modified f-GO.

![Figure 1. Infrared spectra of (a)GO, (b)f-GO, (c)SiO₂, (d)MBI@SiO₂, (e)f-GO-MBI@SiO₂.](image)

3.2 Particle size distribution test

The particle size of the mesoporous SiO₂ microspheres and MBI@SiO₂ were tested with a laser particle size analyzer. The results are shown in figure 2, the particle size D₁₀ of mesoporous SiO₂ microspheres with a cumulative distribution of 10% is 6.428 μm, and the particle size D₉₀ is 31.835 μm, the average particle size Dᵥ is 17.247 μm. After loading the inhibitor, the cumulative distribution of MBI@SiO₂ particles is 10%, the particle size D₁₀ is 6.368 μm, D₉₀ is 45.752 μm, and the average particle size Dᵥ is 21.467 μm. It can be seen that the particle size of the mesoporous SiO₂ microspheres does not change much after the drug is loaded, that is, the loading of the drug does not cause the microspheres to agglomerate or is loaded on the outside of the mesoporous SiO₂ microspheres, make the particle size of the microspheres significantly increased.
3.3 Electrochemical test

In order to compare the corrosion resistance of different proportions of f-GO-MBI@SiO₂ doped PU coatings, pure polyurethane coating, 2wt.%, 5wt.%, 8wt.% ratio doped f-GO-MBI@SiO₂/PU composite coating electrochemical tests were carried out, and the impedance data was analyzed using Gamry Echem Analyst software, the coating thickness is 80 μm-100 μm. Figure 3a and b respectively shows the impedance spectra of pure polyurethane coating, 2wt.% f-GO-MBI@SiO₂/PU, 5wt.% f-GO-MBI@SiO₂/PU, 8wt.% f-GO-MBI@SiO₂/PU. According to the results, compared with the PU coating, the anticorrosion effect of the polyurethane composite coating doped with f-GO-MBI@SiO₂ is significantly improved. Among them, 5wt.% f-GO-MBI@SiO₂/PU composite coating has the highest corrosion resistance, which is two orders of magnitude higher than PU coating. The corrosion resistance of 2wt.% f-GO-MBI@SiO₂/PU, 8wt.% f-GO-MBI@SiO₂/PU composite coating is one order of magnitude higher than that of pure polyurethane coating. This is due to the doping ratio of 2wt.% is too small, the anti-corrosion effect is not significant, and the doping ratio of 8wt.% is too high, leading to partial agglomeration of f-GO-MBI@SiO₂ in the coating system cannot be completely dispersed, the non-uniform coating reduces the barrier effect of corrosive medium penetration.

In order to quantitatively evaluate the corrosion protection performance of the composite coating, the equivalent circuit shown in figure 4 is used to fit the EIS spectrum. The fitting results are shown in table 1, one time constant is selected to fit the corrosive medium according to the EIS spectrum results. \( R_s \) and \( R_g \) represent the solution resistance and the coating resistance, respectively. Generally speaking, the \( R_g \) coating resistance represents the ability of the coating to block the penetration of corrosive ions, and the CPE capacitance value can reflect the anti-permeability performance of the coating, the penetration of corrosive media will increase the dielectric constant of the coating, thereby increasing the CPE [8]. As shown in table 1, the composite coating of 5wt.% f-GO-MBI@SiO₂/PU has the highest
coating resistance and the smallest capacitance value, indicating that when the doping ratio is 5wt.%, the composite coating is the densest, the corrosion protection effect is the best.

Figure 4. Fitting equivalent circuit diagram.

Table 1. Values of each parameter obtained by fitting EIS spectrum.

| coatings            | $R_p$       | $R_s$       | CPE         |
|---------------------|-------------|-------------|-------------|
| PU                  | $3.13 \times 10^9$ | $7.26 \times 10^{-3}$ | $1.31 \times 10^{-9}$ |
| 2wt. % f-GO-MBI@SiO$_2$/PU | $1.31 \times 10^{11}$ | $1.95 \times 10^{-3}$ | $7.4 \times 10^{-11}$ |
| 5wt. % f-GO-MBI@SiO$_2$/PU | $2.5 \times 10^{12}$ | $3.41 \times 10^{-3}$ | $5.46 \times 10^{-13}$ |
| 8wt. % f-GO-MBI@SiO$_2$/PU | $9.63 \times 10^{11}$ | $1.78 \times 10^{-3}$ | $1.91 \times 10^{-11}$ |

Since the electrochemical behavior of low carbon steel corrosion is an active dissolution process, it is necessary to pay attention to the current density $j_{corr}$ and the potential $\phi_{corr}$. As shown in figure 5 and table 2, the self-corrosion current density of the composite coating doped with f-GO-MBI@SiO$_2$ is significantly lower than that of PU, and the self-corrosion potential is also corrected. Indicating that the surface doping of f-GO-MBI@SiO$_2$ significantly improves the corrosion resistance of low carbon steel, and when the doping ratio is 5wt.%, composite coatings have the best corrosion resistance.

Table 2. Self-corrosion current density and self-corrosion potential of the composite coating.

| coatings            | $\phi_{corr}$ (vs.SCE) /V | $j_{corr}$ (A·cm$^{-2}$) |
|---------------------|---------------------------|--------------------------|
| PU                  | -0.69                      | $5.83 \times 10^{-9}$    |
| 2wt. % f-GO-MBI@SiO$_2$/PU | -0.64                   | $3.34 \times 10^{-10}$   |
| 5wt. % f-GO-MBI@SiO$_2$/PU | -0.48                   | $1.91 \times 10^{-11}$   |
| 8wt. % f-GO-MBI@SiO$_2$/PU | -0.57                   | $8.93 \times 10^{-11}$   |

3.4 Resistance to neutral salt spray test
Figure 6 shows the appearance photos of different coatings after continuous exposure for 360 h in neutral salt spray tank. Table 3 shows the width of corrosion spread at scratches of different coatings, the coating thickness is 80 μm-100 μm. After 360 h, the pure PU coating has appeared relatively serious corrosion, with more rust spots on the surface, especially in the scratch area. It indicates that the corrosive medium has penetrated into the interface between the coating and the substrate, resulting in corrosion spread.
The corrosion degree of the composite coating added with f-GO-MBI@SiO₂ is relatively light, except for a small amount of rust on the surface of the composite coating 2wt.% f-GO-MBI@SiO₂, there is no rust on the surface of the composite coating 5wt.% f-GO-MBI@SiO₂, 8wt.% f-GO-MBI@SiO₂. This suggests that the presence of graphene nano container to increase the proliferation of corrosive medium channel, slow down the corrosion process, and when the substrate surface corrosion occurs, MBI molecules in nano container will be released, covalent bonds and coordination bonds combine with metal ions to re-form an insoluble protective film on the damaged metal surface, which can effectively inhibit the corrosion of metals.

Figure 6. Appearance photo of composite coating after 360 h neutral salt spray.

Table 3. Corrosion spread width at scratches after 360 h neutral salt spray of composite coating.

| coatings            | Corrosion spread width at scratch/mm |
|---------------------|--------------------------------------|
| PU                  | 6                                    |
| 2wt.% f-GO-MBI@SiO₂/PU | 5                                    |
| 5wt.% f-GO-MBI@SiO₂/PU   | 1.5                                  |
| 5wt.% f-GO-MBI@SiO₂/PU   | 3                                    |

3.5 Adhesion test
PU, 2wt.%, 5wt.% and 8wt.% proportionly-doped f-GO-MBI@SiO₂ composite coating were tested by pull-out tester. The results are shown in figure 7 and table 4. Compared with pure polyurethane coating, the adhesion of the composite coating doped with f-GO-MBI@SiO₂ has no significant change, it shows that the addition of the drug-loaded nanocontainer has no significant effect on the adhesion between the coating and the substrate.

Figure 7. Pull apart method adhesion photograph of PU,2wt.% f-GO-MBI@SiO₂, 5wt.% f-GO-MBI@SiO₂, 8wt.% f-GO-MBI@SiO₂.

Table 4. Pull apart method adhesion of PU,2wt.% f-GO-MBI@SiO₂, 5wt.% f-GO-MBI@SiO₂, 8wt.% f-GO-MBI@SiO₂.

| coatings            | Adhesion pull apart method/MPa |
|---------------------|--------------------------------|
|                     | 1st   | 2nd   | 3rd   | average |
| PU                  | 16.3  | 15.45 | 14.99 | 15.58   |
| 2wt.% f-GO-MBI@SiO₂/PU | 15.03 | 13.7  | 14.23 | 14.32   |
| 5wt.% f-GO-MBI@SiO₂/PU   | 14.63 | 15.18 | 14.84 | 14.88   |
| 8wt.% f-GO-MBI@SiO₂/PU   | 13.97 | 14.28 | 14.51 | 14.25   |
4. Conclusion
The SiO₂ was used as a carrier to support the corrosion inhibitor 2-mertobenzoimidazole (MBI), and the silane coupling agent GPTS was used as a bridging agent to composite with graphene oxide (GO) to prepare f-GO-MBI@SiO₂ composite nanomaterials, and the composite nanomaterials were added to the polyurethane varnish in different proportions and sprayed onto the surface of low carbon steel. Corrosion resistant performance of the modified polyurethane coating has significantly improved, this is due to the layered structure of the GO effectively increase the corrosion medium penetration to the path of the substrate, the presence of SiO₂ effectively fills the gaps in the coating and the release of corrosion inhibitors can delay the corrosion caused by coating defects. When the doping ratio is 5wt.%, the corrosion resistance of the coating is the best.

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