Preparation and Properties of Polyaniline/Expanded Vermiculite Powder Modified Waterborne Epoxy Resin Anticorrosive Coating Postprint

Authors: Wang Na, Hu Lidong, Sun Miao, Zhang Jing, Wu Hang, WANG Fuhui

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Abstract

Waterborne epoxy anticorrosive coatings were prepared using polyaniline (PANI)-modified expanded vermiculite powder (VMT) as anticorrosive filler. The chemical composition of the anticorrosive filler was characterized by infrared spectroscopy analyzer (IR), and its thermal stability was tested by thermogravimetric analyzer (TG). The effects of different mass fractions of PANI/VMT anticorrosive filler on the anticorrosive performance of waterborne epoxy coatings were investigated by electrochemical impedance spectroscopy (EIS) and salt spray test. The results show that the PANI/VMT anticorrosive filler combines the anodic protection effect of polyaniline (PANI) and the shielding effect of expanded vermiculite powder (VMT), providing good corrosion protection for metal substrates. When the mass fraction of PANI/VMT is 0.5%, the modified waterborne epoxy coating exhibits the best anticorrosive effect.

Full Text

Preparation and Anticorrosion Performance of Polyaniline/Vermiculite Modified Waterborne Epoxy Coatings

WANG Na[1,2], **HU Lidong**[1], **SUN Miao**[1], **ZHANG Jing**[1], **WU Hang**[3], **WANG Fuhui**[3]

[1]School of Materials Science and Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China
[2]School of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China
[3]State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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To whom correspondence should be addressed, Tel: 13840257976, E-mail: iamwangna@sina.com

Abstract

Waterborne epoxy anticorrosion coatings were prepared using polyaniline/vermiculite (PANI/VMT) as a corrosion-inhibiting pigment. The chemical composition of the pigment was characterized by Fourier-transform infrared spectroscopy (FTIR), and its thermal properties were evaluated by thermogravimetric analysis (TGA). The anticorrosion performance of waterborne epoxy coatings containing different mass fractions of PANI/VMT pigment was investigated through electrochemical impedance spectroscopy (EIS) and salt spray testing. The results demonstrate that the PANI/VMT pigment combines the anodic protection capability of polyaniline (PANI) with the barrier properties of vermiculite (VMT), providing effective corrosion protection for metal substrates. The modified waterborne epoxy coating exhibited optimal anticorrosion performance when the PANI/VMT mass fraction was 0.5%.

Keywords: materials failure and protection, waterborne epoxy, polyaniline, vermiculite, anticorrosion coating

Introduction

Vermiculite (VMT) is a layered silicate clay mineral with a structure similar to montmorillonite, but with higher specific surface area, greater interlayer exchange capacity, and superior chemical inertness, all at a lower cost. These characteristics have led to widespread applications in wastewater treatment, composite materials, refractory materials, and inorganic films. Polyaniline (PANI), a mainstream conductive polymer material, has gained attention in recent years as an excellent anticorrosion material. The reduction of oxygen on PANI coatings compensates for the charge consumed by metal dissolution, thereby stabilizing the potential of the passive state and reducing the corrosion rate of the metal. The combination of PANI with inorganic fillers integrates anodic protection with barrier effects, improving the anticorrosion capability of coatings. This study modifies vermiculite with polyaniline to prepare PANI/VMT-modified waterborne epoxy anticorrosion coatings, investigating the influence of different pigment mass fractions on coating performance.

1. Experimental Methods

1.1 Preparation of PANI/VMT Pigment The raw materials included expanded vermiculite powder (100 mesh), aniline (99.5%), hydrochloric acid (36-38%), and ammonium persulfate (98%). First, 5.0 g of vermiculite powder was purified by treatment with 10% HCl solution, then added to 200 mL of 2% HCl solution. After adding 2 mL of aniline, the mixture was ultrasonicated for 2 h to ensure adequate dispersion. The solution was then placed in a magnetic stirrer at 25°C, and 6 g of ammonium persulfate was added to initiate polymerization for 5 h. Following reaction completion, the product was filtered and washed repeatedly with 2% HCl solution and distilled water until the filtrate became clear. The filter cake was dried in a vacuum oven at 60°C for 24 h and ground to obtain the PANI/VMT pigment.

1.2 Preparation of Modified Anticorrosion Coatings The primary materials were waterborne epoxy resin (AR555) and amino curing agent (Aq419). The epoxy resin and curing agent were weighed at a 4:1 mass ratio and diluted separately with distilled water. The diluted epoxy resin was mixed with the prepared pigment (at mass fractions of 0.3%, 0.5%, 0.7%, and 1.0%) and subjected to ball milling to ensure uniform dispersion. The diluted curing agent was then added, and the mixture was stirred magnetically to prepare the PANI/VMT-modified waterborne epoxy anticorrosion coating.

Q235A carbon steel substrates (50 mm × 50 mm × 2 mm) were sandblasted and cleaned with acetone and anhydrous ethanol to remove sand, grease, and moisture. Coatings were applied by air spraying onto the prepared substrates and cured at room temperature for 7 days to obtain the final modified coatings.

1.3 Characterization Methods The chemical composition of the pigment was analyzed using a Nicolet IR560 attenuated total reflectance infrared spectrometer (IR). Thermal gravimetric analysis (TGA) was performed on a STA449C thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Metrohm AUTOLAB 84362 electrochemical workstation at open-circuit potential. Coated specimens with a thickness of 30 ± 3 µm were mounted in an electrochemical cell with an exposed area of approximately 9.6 cm^2, using 3.5% NaCl solution as the corrosive medium. A three-electrode system was employed: saturated calomel electrode (SCE) as reference, platinum electrode as counter, and the coated specimen as working electrode. Impedance spectra were recorded using Nova 1.8 software over a frequency range of 100,000 Hz to 0.1 Hz with a 10 mV sinusoidal perturbation.

Salt spray testing was performed using a YWα/Q-150 corrosion test chamber according to the following conditions: temperature 35 ± 2°C, salt spray pressure 0.5-1.7 kg/cm^2, 5% NaCl solution, continuous spraying for 600 h, with periodic observation of surface changes.

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2. Results and Discussion

2.1 FTIR Analysis of PANI/VMT Figure 1 [Figure 1: see original paper] presents the FTIR spectra of the PANI/VMT pigment, where curves a, b, and c correspond to VMT, PANI, and PANI/VMT, respectively. The spectrum of PANI/VMT (curve c) exhibits characteristic absorption peaks of both VMT (curve a) and PANI (curve b). The peak at 683 cm^{-1} corresponds to Al-O stretching vibrations of VMT, the strong absorption at 997 cm^{-1} is attributed to Si-O-Si characteristic peaks of silicate-type VMT, and the weak peak at 3675 cm^{-1} represents the Mg_3OH group characteristic of trioctahedral minerals like VMT. The broad absorption at 1129 cm^{-1} indicates protonation of C-H in PANI, the peak at 1567 cm^{-1} is assigned to C=C stretching in the benzene ring structure, and the characteristic absorption at 3444 cm^{-1} confirms the presence of $-NH_2$ groups in PANI/VMT. The enhanced intensity at 1567 cm^{-1} results from conjugation between the benzene ring and $-NH_2$ groups. Slight shifts in the characteristic peaks compared to pure PANI suggest strong interactions between PANI and VMT in the pigment.

2.2 Thermogravimetric Analysis of PANI/VMT Figure 2 [Figure 2: see original paper] shows the TGA curves of VMT (curve a) and PANI/VMT pigment (curve b). VMT exhibits a total mass loss of approximately 5.3% between 40°C and 800°C, primarily due to evaporation of free water and interlayer structural water. As shown in the DTG curve, the thermal degradation of PANI/VMT occurs in three stages: (1) below 100°C, dehydration with ~2.0% mass loss; (2) around 230°C, decomposition of non-chemically bonded PANI with ~3.7% mass loss; and (3) at approximately 535°C, decomposition of intercalated and chemically bonded PANI with ~8.2% mass loss. The total mass loss of PANI/VMT throughout the test was approximately 22.4%.

2.3 Electrochemical Analysis of Coating Specimens The effect of different PANI/VMT mass fractions on the anticorrosion performance of waterborne epoxy coatings was evaluated to determine the optimal formulation. Specimens I, II, III, IV, and V correspond to neat waterborne epoxy coating and PANI/VMT-modified coatings with pigment mass fractions of 0.3%, 0.5%, 0.7%, and 1.0%, respectively. Figures 3 [Figure 3: see original paper]-7 [Figure 7: see original paper] present the EIS spectra (Nyquist and Bode plots) for these coatings after immersion times of 0 h, 24 h, 360 h, 720 h, and 1440 h in 3.5% NaCl solution.

At 0 h immersion, all coatings exhibited high impedance values, with |Z| showing a linear relationship with frequency in Bode plots and phase angles approaching -90° over a wide frequency range. The low-frequency impedance values ($|Z|_{0\cdot 1}$) were 6.47$×10^{8}$ $\Omega \cdot cm^2$, 5.96$×10^{8}$ $\Omega \cdot cm^2$, 2.07$×10^{9}$ $\Omega \cdot cm^2$, 1.89$\times10^{9}$ $\Omega\cdot \mathrm{cm}^2$, and 8.95$\times10^{8}$ $\Omega\cdot \mathrm{cm}^2$ for specimens I-V, respectively. Specimen III (0.5% PANI/VMT) showed the highest $|Z|_{0\cdot 1}$ value, indicating optimal barrier properties at the initial stage due to the layered structure of PANI/VMT hindering corrosive medium penetration.

With prolonged immersion, the |Z| vs. frequency and phase angle curves in the Bode plots decreased, indicating increased coating capacitance and decreased resistance, which reflects penetration of corrosive species and gradual coating degradation. Water, O_2, and Cl^- ions diffuse through coating defects and pores to the metal surface, initiating redox reactions.

The reaction products diffuse into the electrolyte, creating ion exchange currents corresponding to the period from 24 h to 720 h immersion. For specimens I (neat epoxy) and II (0.3% PANI/VMT), the impedance |Z| in the low-frequency region showed minimal decrease and maintained a plateau-like behavior before decreasing linearly with frequency after reaching a characteristic frequency. In contrast, specimens III, IV, and V exhibited less distinct characteristic frequencies, indicating that the dispersed lamellar structure of PANI/VMT effectively blocked corrosive medium penetration, preserving shielding capability even after prolonged immersion.

After 720 h immersion, the low-frequency impedance values ($|Z|_{0\cdot 1}$) were 1.09$\times10^{7}$ $\Omega\cdot \mathrm{cm}^2$, 1.49$\times10^{7}$ $\Omega\cdot \mathrm{cm}^2$, 1.39$\times10^{8}$ $\Omega\cdot \mathrm{cm}^2$, 1.19$\times10^{8}$ $\Omega\cdot \mathrm{cm}^2$, and 7.20$\times10^{7}$ $\Omega\cdot \mathrm{cm}^2$ for specimens I-V, respectively.

At 1440 h immersion, specimens III, IV, and V showed impedance |Z| decreasing linearly with frequency after reaching the characteristic frequency in the medium-low frequency region, similar to the behavior of specimens I and II at 360 h and 720 h. The $|Z|_{0\cdot 1}$ values were 1.60$\times10^{6}$ $\Omega\cdot \mathrm{cm}^2$, 2.01$\times10^{6}$ $\Omega\cdot \mathrm{cm}^2$, 7.37$\times10^{6}$ $\Omega\cdot \mathrm{cm}^2$, 6.13$\times10^{6}$ $\Omega\cdot \mathrm{cm}^2$, and 2.98$\times10^{6}$ $\Omega\cdot \mathrm{cm}^2$, respectively. This indicates that electrolyte penetration had reached saturation and contacted the metal substrate, causing corrosion and abrupt impedance changes. However, as shown in Figure 3a, the neat epoxy coating after 1440 h exhibited a near-semicircular capacitive arc in the high-frequency region of the Nyquist plot, suggesting limited diffusion processes. The characteristic frequency shifted to the medium-frequency region (Figure 3b), and two time constants appeared in the low-frequency region (Figure 3c), indicating coating delamination and blistering. In contrast, pigmented coatings showed significantly reduced impedance and phase angle values but no two-time-constant behavior or Warburg impedance, indicating that while shielding effectiveness decreased, coating failure had not yet occurred.

These results demonstrate that specimen III (0.5% PANI/VMT) maintained the highest impedance values at all time points, indicating optimal anticorrosion performance.

For further investigation, coatings modified with 0.5% VMT alone and 0.5% PANI alone were compared with the 0.5% PANI/VMT coating. Figure 8 [Figure

8: see original paper] shows the variation of low-frequency impedance $|Z|_{0\cdot 1}$ with immersion time. All pigmented coatings exhibited higher $|Z|_{0\cdot 1}$ values than the neat epoxy coating, with the PANI/VMT coating showing superior performance compared to both VMT-only and PANI-only modifications.

VMT is a chemically stable, water-insoluble, inert filler resistant to decomposition by corrosive media, providing effective filling with minimal surface defects. These properties create a dense coating structure with enhanced strength, while the characteristic lamellar structure dispersed in the epoxy matrix obstructs the diffusion pathways of corrosive ions, reducing permeation of water, oxygen, and ions. This enhanced physical barrier effect improves anticorrosion performance.

The PANI/VMT pigment is not a simple mechanical blend but rather involves in-situ polymerization of aniline on the VMT surface, creating chemical bonding and stronger adsorption. PANI provides adhesion, improving compatibility between VMT and the epoxy matrix, and acts as an intermediary with the metal substrate. Through reversible redox reactions with oxygen, PANI forms a dense oxide film on the metal surface (passivation) while transitioning from its conductive intermediate oxidation state to a reduced state. This redox reaction compensates for charge consumption by metal dissolution, stabilizing the passive potential and reducing corrosion rates.

Figure 9 [Figure 9: see original paper] shows Tafel polarization curves after 24 h immersion. The 0.5% PANI/VMT coating (curve c) exhibited the highest corrosion potential (-0.26 V) compared to -1.08 V for the neat epoxy coating (curve a). Higher corrosion potential indicates superior corrosion resistance. Table 1 presents corrosion potential and corrosion rate data, with the 0.5% PANI/VMT coating showing the lowest corrosion rate (2.10$×10^{-5}$ mm/a). These results confirm that PANI/VMT addition enhances corrosion potential and reduces corrosion rate. The proposed anticorrosion mechanism is illustrated in Figure 10 [Figure 10: see original paper].

2.4 Salt Spray Testing Figure 11 [Figure 11: see original paper] compares the corrosion resistance of neat epoxy coating (a), VMT-modified (b), PANI-modified (c), and PANI/VMT-modified coatings with pigment mass fractions of 0.3% (d), 0.5% (e), 0.7% (f), and 1.0% (g) after 600 h salt spray exposure. Corrosion spots and blistering were observed to varying degrees. The neat epoxy coating (a) showed obvious rust and corrosion spots, while specimens b, c, and d exhibited slight blistering. Specimen e (0.5% PANI/VMT) showed no significant corrosion or blistering, whereas specimens f and g displayed severe blistering, with partial coating detachment in specimen g. These results confirm that the 0.5% PANI/VMT coating possesses the best salt spray resistance.

3. Conclusion

The PANI/VMT pigment effectively combines the anodic protection, passivation, and barrier properties of polyaniline and vermiculite, significantly hindering diffusion of corrosive media to the metal substrate and substantially improving the anticorrosion performance of waterborne epoxy coatings. The modified coating achieves optimal anticorrosion performance at a PANI/VMT mass fraction of 0.5%.

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