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Effect of carbon nanotubes on the corrosion resistance of water-borne acrylic coatings

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ABSTRACT

The effects of multiwalled carbon nanotubes (MWCNTs) on the adhesion strength and corrosion resistance of the acrylic nanocomposite coatings were evaluated on Q235 substrates via pull-off tests and electrochemistry measurements (EIS, LEIS). Addition of MWCNTs to the acrylic resulted in an up to ~50% increase in the adhesion strength. After 36 h of immersion in 3.5 wt% NaCl, the coating resistance of the native acrylic coating was 235.8 Ω cm^2, whereas those of the nanocomposite coatings containing 0.5 and 1 wt% MWCNTs were 1.36 × 10^5 and 9.27 × 10^7 Ω cm^2, respectively. LEIS analysis indicated that the addition of MWCNTs increased the adhesion strength and retarded the delamination. The results demonstrated the positive effects of the incorporation of MWCNTs on the anticorrosive ability of the coatings.

1. Introduction

Corrosion of iron and its alloys causes a yearly loss of billions of dollars, and approximately 90% of all metallic surfaces are protected with organic coatings [1–4]. Traditional coatings are mostly based on solvents and contain high levels of volatile organic compounds [5,6]. Water-based coatings, such as acrylic latex, are more environmentally friendly and have gained increasing popularity over the years [7,8]. However, dense crosslinking of waterborne coating is difficult, thereby limiting its corrosion resistance and durability.

Improving the anticorrosive ability of water-based coating is a pivotal issue for both scientific and industrial communities. Pigments are a class of important components, which can significantly affect the nature of coatings. Addition of nanoparticle pigments, can produce beneficial effects on corrosion resistance and mechanical properties of organic coatings at the comparatively low loadings because of the inherent small sizes and the particle morphologies [9–11].

Carbon nanotubes (CNTs) are excellent reinforcing agents for polymer nanocomposites because of their ultrahigh tensile strength, high aspect ratio, as well as high thermal and electrical conductivity [12–14]. Frankel [15] and Jeon [16] found that incorporation of CNTs improved wear resistance, adhesion strength, and corrosion resistance of solvent-based epoxy coatings. To best of our knowledge, the correlation between the incorporation of CNTs and the corrosion performance of waterborne coating remains unclear.

Herein, the waterborne acrylic coating with different contents of multiwalled CNTs (MWCNTs) were prepared on Q235 steel substrates. The adhesion strength and the corrosion resistance of the coated samples were systematically investigated.

2. Materials and experiment

The acrylic resin (DL 1065) was obtained from D LIAN (China Beijing). Prior to painting, the commercially available Q235 steel panels were cut into 50 mm × 75 mm pieces and then abraded with SiC paper to 240 grit. The substrates were then cleaned ultrasonically in acetone and air drying. The MWCNTs (L-MWNT-1020) were purchased from Shenzhen Nanotech Port Company, China. The MWCNTs are 10–20 nm in diameter and 5–10 μm in length. Each nanotube has 7–15 walls with bulk density of 0.03-0.16 g/cm^3. The MWCNTs were dispersed in the acrylic resin by ball-milling for approximately 1 h. The Q235 substrates were coated with acrylic resins containing 0.5, 1, and 3 wt% MWCNTs. And a blank sample was used for comparison. All coatings were cured at room temperature for two days, and then at 50 °C for three days. The average thickness of the obtained coating was 20 ± 2 μm for electrochemistry measurements and 40 ± 4 μm for other analyses. Scratches (1-mm long and 120-μm wide) were made using a utility knife for local electrochemical impedance spectroscopy

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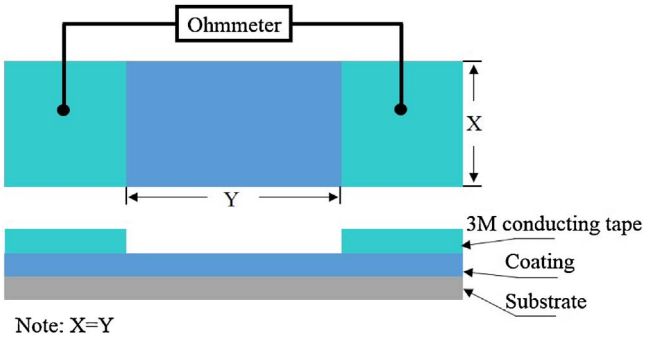

Fig. 1. Surface resistance measuring scheme.

(LEIS).

The surface morphologies of the coating samples were observed by scanning electron microscopy (SEM) (Quanta 250). The adhesion strength was determined by pull-off measurements using PosiTest drawing type adhesion tester according to ISO 4624. EIS measurements were conducted in 3.5 wt% NaCl solution with a PARSTAT 2273 system, over the frequency range of 10^5 Hz to 10^{-2} Hz at open circuit potential, with a 20 mV potential perturbation. A three-electrode arrangement was used, consisting of a saturated calomel electrode as reference electrode, a platinum electrode as counter electrode, and the coated sample as the working electrode. The area of exposure of the working electrode was 3.14 cm^2.

As shown in Fig. 1, according to the YlVIS2503, an ohmmeter and a 3 M conducting tape (aluminum or copper foil) were used for surface resistance testing.

LEIS measurements were performed on coated specimens that were immersed in 3.5 wt% NaCl solution through a PAR Model 370 Scanning Electrochemical Workstation. Besides, the test solution for LEIS measurements was 0.001 M NaCl solution. The microprobe was stepped over a designated area of the electrode surface. The scanning took the form of a raster in x–y plane. The step size was controlled to obtain a plot of 32 lines × 11 lines. The AC disturbance signal was 100 mV, and the disturbance frequency for impedance measurements was fixed at 5 kHz. All LEIS measurements were carried out at ambient temperature (~22 °C). Each test was performed at least twice to confirm the repeatability.

3. Results and discussion

Fig. 2 shows that the coating was uniform and defect free. Also, the MWCNTs particles were well dispersed in the polymer matrix.

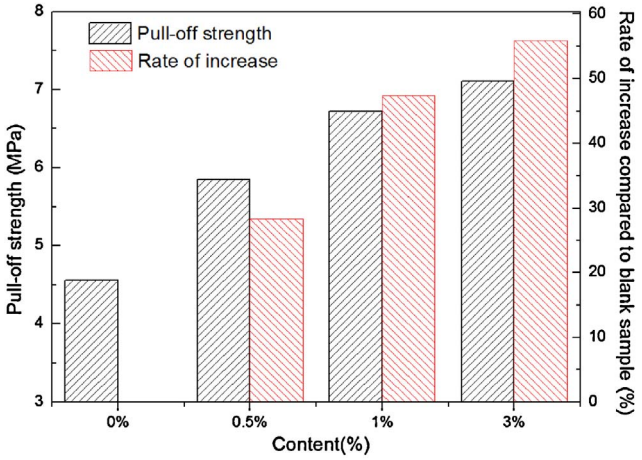

Fig. 3. Pull-off strength of the coatings on Q235 panels and rate of increase compared to blank sample.

Results of the adhesion tests are shown in Fig. 3. Addition of MWCNTs to the acrylic matrix resulted in an up to 56% increase in the adhesion strength, indicating an enhanced bonding between the nanocomposite coating and the metal substrate. The interfacial bonding between the coating and substrate can be affected by the curing process because of the shear stress induced at the coating/substrate interface by the residual stress in the coating [17,18]. The incorporation of MWCNTs is expected to relax the residual stress in the polymer matrix by shearing the weakly bound carbon aggregates against the matrix. Thus, the adhesion strength of the coatings is improved with the increasing level of MWCNTs [15].

The protective capacity of the acrylic nanocomposite coatings over substrates was investigated using EIS in a 3.5 wt% NaCl solution. Fig. 4 shows the electrochemical behavior of the coatings under different immersion times. A water-based acrylic resin was used in this paper, and its impermeability is weaker than the traditional solvent-based resin based on the special water-based resin film curing principle [19]. Thus, the coating will have more defects, such as high porosity. Meanwhile, the coating is very thin, thus, the coating exhibits the two time constants at the initial of immersion.

The EIS data were fitted using equivalent circuit model shown in the inset of Fig. 5a. R_s is the solution resistance. R_{po} and C_c represent the pore resistance and the coating capacitance, respectively. R_{ct} and C_{dl}

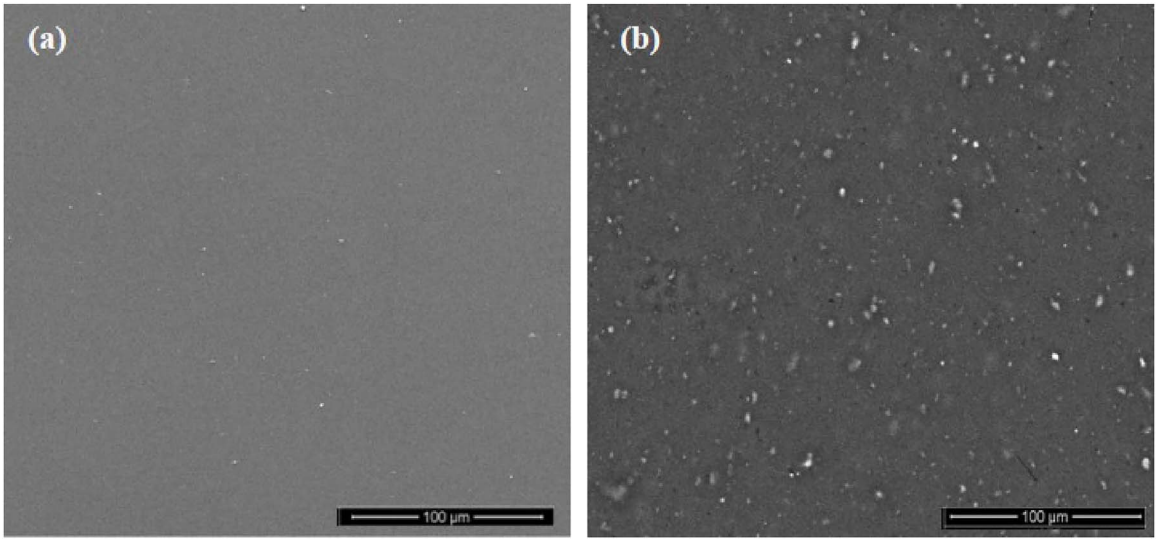

Fig. 2. SEM micrograph of (a) blank sample and (b) nanocomposite coating with 1 wt% CNTs.