Research Article

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Hydrophobicity and corrosion resistance of waterborne fluorinated acrylate/silica nanocomposite coatings

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Abstract: This study aims to improve the hydrophobic properties and corrosion resistance of fluorinated acrylate coatings. The surface of nano-SiO₂ was modified by the silicone coupling reagent (KH-570), and the reactive functional groups were introduced to modify fluorinated acrylates. The functionalized SiO₂-modified waterborne fluorinated acrylate emulsion was prepared by free polymerization with dual initiators. The structure of the polymer was analyzed by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectro-meter (¹H-NMR), X-ray photoelectron spectroscopy (XPS) and Waters gel chromatography (GPC). The properties of the films and coatings were analyzed by contact angle, atomic force microscopy, scanning electron microscopy, and electrochemical analysis. The results showed that the contact angle reached 120° when the SiO₂ content was 3%, the electrochemical impedance value reached $1.49 \times 10^7 \Omega \cdot \text{cm}^2$, and the pencil hardness was 3H.

Keywords: nano-SiO₂, acrylate, fluoropolymer, hydrophobic, anticorrosive

1 Introduction

Metal products are susceptible to corrosion by corrosive substances in the environment (water vapor, Cl[−], etc.), which not only wastes resources and affects product quality but also reduces service life (1). The organic coatings effectively slow down the corrosion rate of metal products, which include epoxy resin, polyurethane, acrylic resin, etc. The waterborne coatings use water as the solvent or dispersion medium and water-soluble resins as the film-forming substances (generally waterborne epoxy esters, waterborne polyurethanes, and waterborne acrylates). Due to the low production cost, nontoxic, harmless, and nonvolatile organic solvents, waterborne coatings conform to the theme of green environmental protection and attract intensive attention in recent years (2). Waterborne acrylates have the characteristics of low cost, high film transparency, and good gloss, but the shortcomings of the traditional acrylic resins that are “hot and cold and brittle” greatly limit their application range (3). Nanomaterials are successfully applied to the modification of acrylate due to their special anti-ultraviolet, anticorrosion, self-cleaning, high strength and toughness, good electrostatic shielding effect, and antibacterial function (4). Among them, inorganic nano-SiO₂ particles possess many unique properties, such as a large specific surface and strong hydrophilicity. The molecular structure of SiO₂ is very different from that of the polymers (5). Therefore, the compatibility of the inorganic nano-SiO₂ particles and organic polymers is very different, and the stability after mixing is very poor, resulting in delamination.

The introduction of inorganic nanomaterials into polymers requires some methods to modify the surface of the inorganic particles, and the surface of the inorganic nano-SiO₂ particles is usually modified with organic materials such as alkoxysilanes, and silane coupling agents. Jiao et al. (6) prepared waterborne acrylic resin by emulsion polymerization and modified it with 2-(3,4-epoxy)ethyltriethoxysilane (KH-567). The influences of KH-567 on the properties of the waterborne acrylic resins were investigated

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from the aspects of mechanical properties, thermal stability, and hydrophobicity. Harb *et al.* (7) initiated the polymerization of methyl methacrylate (MMA) by benzoyl peroxide (BPO), and 3-(trimethoxysilyl) propyl methacrylate was hydrolyzed and condensed by tetraethyl orthosilicate (TEOS) to form nanosilicon materials. Two different substrates were added in the PMMA–siloxane–silica hybrid material, and the electrochemical impedance spectroscopy (EIS) tests showed that the enhanced hybrid coating had a very effective anticorrosion barrier. Lei *et al.* (8) prepared fluorine-containing silicone resin polymers with different light absorption doses by solution polymerization, which comprised high ultraviolet absorption performance and good thermal stability. The combination of fluorine and silicon greatly improved the hydrophobicity of the coating, and the protective effects of acrylate, organic fluorine, and organic silicon were better integrated, thus enhancing weather resistance. Dong *et al.* (9) modified the surface of graphene oxide by the hydrolysis of tetraethoxysilane (TEOS) to prepare a silica–graphene oxide nanohybrid material and then added it as a reinforcing material to acrylic resin to prepare acrylic nanocomposite material. Although a lot of work was done on the preparation of polymer/silica nanocomposites, there were few studies on the graft modification of the nano-SiO₂ surface with fluorine-containing acrylic monomers. In addition, there was also relatively little research on its use in the anticorrosion hydrophobicity of the coatings.

In this study, KH-570 was used to modify the surface of nano-SiO₂ to obtain functionalized nano-SiO₂, and a dual initiator was used to initiate the radical polymerization of the fluorine-containing acrylic monomers. Finally, the functionalized nano-SiO₂-modified waterborne fluorinated acrylate (SiO₂@AR-F) emulsion was prepared. The hydrophobicity and corrosion resistance of the coating were studied by contact angle test and electrochemical analysis. The grafting of fluorinated acrylate segments to the functionalized SiO₂ surface not only effectively improved the surface roughness of the coating but also fully filled the gaps of the coating by SiO₂ particles, thereby improving the hydrophobicity and anticorrosion ability of the coating.

2 Materials and methods

2.1 Materials

N,N-Dimethylethanolamine (DMEA), propylene glycol methyl ether acetate (PMA), isobornyl methacrylate (IBOMA), and

hydroxypropyl acrylate (HPA) were purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin). MMA, acrylic acid (AA), and butyl acrylate (BA) were purchased from Sinopharm Chemical Reagent Company (Shaanxi). Tridecafluorooctyl methacrylate (FMA) was obtained from Guangdong Wengjiang Chemical Reagent Company (Guangdong). Nano-SiO₂, BPO, and tert-butyl perbenzoate (TBPB) were purchased from Shanghai Macleans (Shanghai). KH-570 was purchased from Jiangsu Chenguang Coupling Agent Company (Jiangsu).

2.2 Synthesis of functionalized nano-SiO₂

To the absolute ethanol/water (mass ratio 3:1) mixed solution, 10 g of nano-SiO₂ was added and ultrasonically dispersed for 2 h, and 20% silane coupling agent KH-570 was then added. The mixed solution of absolute ethanol and pH 3.5 oxalic acid (mass ratio 1:1) was added and ultrasonically dispersed for 1 h, and then the flask was placed in a 70°C constant temperature water bath and mechanically stirred for 4 h. Finally, the obtained emulsion was centrifuged at 2,000 rpm and washed with a mixture of ethanol and deionized water three times to remove KH-570 and by-products physically adsorbed on the surface of nano-SiO₂. The products were placed in a vacuum drying oven at 60°C and dried for 6 h to obtain a functionalized surface-modified nano-SiO₂ powder.

2.3 Synthesis of functionalized SiO₂@AR-F

In this experiment, the functionalized SiO₂@AR-F was synthesized by using dual initiators to initiate free radical polymerization. To 28 g of solvent PMA, 1% (0.27 g) functionalized nano-SiO₂ was added and ultrasonically dispersed for 1 h to completely disperse nano-SiO₂ in the solvent. The flask was then placed in an oil bath for mechanical stirring. When the temperature reached 80°C, acrylic monomers (10 g of MMA, 8 g of BA, 3 g of AA, 2 g of HPA, 1 g of IBOMA, and 1.56 g of FMA) and initiator BPO (1% of the total monomer) were added dropwise to the flask within 1 h. After reaction for 3 h, the temperature was raised to 110°C, and then the high-temperature initiator TBPB (1% of the total monomer) was added to continue the reaction for 2 h. The flask cooled to about 50°C, and 2.4 g of DMEA was added to neutralize the carboxyl group in the product (neutralization degree was 0.8). Then a certain amount of water was added and emulsified under high-speed stirring to obtain a functionalized SiO₂@AR-F (Scheme 1).

Scheme 1: Preparation of $\text{SiO}_2@AR-F$.

While keeping other conditions unchanged, the dosage of functionalized nano- SiO_2 was changed to 0%, 1% (0.27 g), 2% (0.54 g), 3% (0.81 g), and 4% (1.08 g), respectively. And the prepared emulsions were marked as AR-F (Fluorinated Acrylate), 1% $\text{SiO}_2@AR-F$, 2% $\text{SiO}_2@AR-F$, 3% $\text{SiO}_2@AR-F$, and 4% $\text{SiO}_2@AR-F$.

Preparation of the coating: Add a certain amount of modified emulsion, pigments and fillers, and deionized water into the beaker. Stir at high speed for 1 h to make it fully dispersed. According to the GB/T1727-1992 standard, spray the coating evenly on the tinplate polished with sandpaper and cure it at room temperature (11).

2.4 Preparation of films and coatings

Film preparation: Accurately weigh 20 g of emulsion, pour it on a polytetrafluoroethylene plate, and dry it at room temperature for 7 days to obtain a polymer film. Then put it in the dry box (10).

2.5 Characterization

The structure of SiO_2 , modified SiO_2 , and $\text{SiO}_2@AR-F$ was characterized by Fourier transform infrared spectroscopy (VECTOR-22, Bruker, Germany), and the scanning range was $400-4,000\text{ cm}^{-1}$. The $^1\text{H-NMR}$ of $\text{SiO}_2@AR-F$ was

tested by 600 MHz nuclear magnetic resonance spectrometer (AVANCE NEO, Bruker, Germany). The stability of the emulsion was measured using a stability analyzer (Turbiscan Lab). The measuring temperature is 25°C, the measuring time is 1 h, and near infrared light λ is 880 nm. The particle size and distribution of the emulsion were measured with a nanoparticle size surface potential analyzer (Malvern, Tianjin). The test temperature was 25°C, the laser angle was 90°, and the test laser wavelength was 633 nm. A thermogravimetric analyzer (TGA-Q500, TA Company, United States) was used to measure the thermal stability of the film. The atmosphere was N₂, the temperature range was 25–600°C, and the heating rate was 10°C·min⁻¹. The atomic force microscope (AFM; SPA400, Japan Seiko, Japan) was used to observe and analyze the microscopic surface morphology of the coating. The sample size was 1 cm × 1 cm. The molecular weight of the polymer was measured using Waters gel chromatography GPC (E2695, Waters, Shanghai). The contact angle of the film was measured with a contact angle measuring instrument (KRÜSS, Germany). The field emission scanning electron microscope (SEM; FEI Verios 460, Netherlands) was used to analyze the corrosion morphology of the coated tinplate. Electrochemical workstation (Princeton) was used to conduct electrochemical analysis of samples. Test conditions: Platinum electrode was used as an auxiliary electrode, calomel electrode was used as a reference electrode, sample was used as a working electrode, area was 1 cm², and electrolyte was 3.5% NaCl aqueous solution (12). Impact resistance was measured according to GB/T1732-1993 “Coating Film Impact Resistance Test Method” (13). Pencil hardness was measured according to GB/T6739-2006

“Pencil Method for Color Paint and Paint Film” (14). Adhesion was measured according to GB/T9286-1998 “Coating and Coating Film Cross-cut Test” (15).

3 Results and discussion

3.1 FTIR and ¹H-NMR analysis

Figure 1a shows the FTIR spectra of SiO₂, modified SiO₂, and SiO₂@AR-F. The peak at 1,623 cm⁻¹ was assigned to the flexural vibration absorption peak of H–O–H, which was attributed to the presence of water adsorbed on the surface of the nano-SiO₂ particles. There was a peak at 1,710 cm⁻¹ corresponding to C=O stretching vibration in the modified SiO₂, which proved that KH-570 was successfully used to modify the surface of SiO₂. The C=C stretching vibration peak of SiO₂@AR-F at 1,623 cm⁻¹ disappeared, proving that the radical polymerization reaction was basically completed. The peak from 1,033 to 1,200 cm⁻¹ was ascribed to the stretching vibration peak of Si–O–Si, and the peak at 470 cm⁻¹ was related to the bending vibration peak of Si–O (16).

Furthermore, ¹H-NMR measurement was conducted to further investigate the structure of SiO₂@AR-F, as shown in Figure 1b. The peak with a chemical shift of 1.06 ppm (a) was the proton of the terminal –CH₃. The chemical shift of 2.35 ppm (b) was assigned to the proton peak of –CH₂–. The peak at 2.50 ppm (c) was due to the solvent peak of DMSO. The chemical shift of 3.46 ppm (d)

Figure 1: FTIR of SiO₂, modified SiO₂, and SiO₂@AR-F (a) and ¹H-NMR of SiO₂@AR-F (b).

referred to the proton peak of $-\text{CH}_2-$ beside the ester group. The peak at 4.35 ppm (e) was ascribed to the proton peak of $-\text{CH}_2-$ next to the terminal hydroxyl group. There was no proton peak of the carbon-carbon double bond at the chemical shift of 5.0–7.0 ppm, which proved that the radical polymerization reaction was basically completed.

3.2 Particle size and stability analysis

Figure 2 shows the particle size distribution and stability analysis of the emulsion. The graft polymerization of fluorinated acrylate on the surface of nano- SiO_2 significantly increased the particle size and distribution of the emulsion. The particle size of the emulsion was 52.28, 85.93, 171.7, 101.7, and 137.3 nm when the SiO_2 addition amount was 0%, 1%, 2%, 3%, and 4%. The modified nano- SiO_2 had different hydrophilicity and hydrophobicity. With the graft polymerization of fluorinated acrylate, the polymer gradually agglomerated on the surface, the degree of molecular chain entanglement and molecular chain length increased, and the particle size of the emulsion increased.

Turbiscan stability index (TSI) monitors the coalescence kinetics in the sample with aging time. In a certain aging time, the higher the TSI value is, the worse the stability of the sample is. TSI parameter took into account all the processes occurring in the sample (sediment and clear layer thickness, and particle settling process), and

the TSI value was obtained through their average. The coefficient was calculated as follows (17):

$$\text{TSI} = \sqrt{\frac{\sum_{i=1}^n (X_i - X_{\text{BS}})^2}{n - 1}} \quad (1)$$

where X_i is the average backscattering for each minute of measurement, X_{BS} is the average of X_i , and n is the number of scans.

As shown in Figure 2b, the TSI value of the emulsion showed a trend of first increase and then flatten as the time increased, indicating that the emulsion became stable after a certain period of aging. The relationship between the stable TSI value of the emulsion with different SiO_2 contents was $1\% \text{ SiO}_2@AR-F \geq 2\% \text{ SiO}_2@AR-F \geq 4\% \text{ SiO}_2@AR-F \geq 3\% \text{ SiO}_2@AR-F \geq AR-F$. Among them, the fluorinated acrylate without SiO_2 had the best stability. The stability of the emulsion gradually decreased as the content of SiO_2 increased. When the content of SiO_2 was 3%, the stability of the emulsion was the best. The addition of nanomaterials improved or affected the stability of the emulsion. Too much SiO_2 was difficult to disperse in water, resulting in precipitation.

3.3 Thermogravimetry (TGA) and molecular weight (GPC) analysis

The thermal stability of the sample film was evaluated by TGA (differential TGA) and DTG (derivative thermogravimetry), and the results are shown in Figure 3. $T_{10\%}$

Figure 2: Emulsion particle size distribution (a) and emulsion stability (b).

Figure 3: Different SiO₂ content: (a) TGA and (b) DTG.

represents the temperature at which the system mass loss is 10%, providing a representation of the initial degradation temperature. $T_{50\%}$ represents the temperature at which the system mass loss is 50%, and $T_{\max}$ refers to the temperature of the maximum mass loss rate in the range of test temperature (18). $T_{10\%}$, $T_{50\%}$, and $T_{\max}$ of different SiO₂ contents are listed in Table 1. The addition of SiO₂ improved the thermal stability of the polymer, and an excessive SiO₂ content in the sample reduced the thermal stability. Among them, the 3% SiO₂@AR-F sample showed the best thermal stability. Compared with the samples without SiO₂, $T_{10\%}$ was increased from 185.6°C to 186.3°C, $T_{50\%}$ was increased from 367.5°C to 376.1°C, and $T_{\max}$ was increased from 380.9°C to 389.1°C, which was due to the high bond energy of Si–O and the network structure containing Si–O, thus effectively slowing down the molecular decomposition rate of the polymer (19).

In addition, the GPC data of the nano-SiO₂-modified fluorinated polyacrylate is shown in Figure 4. The number average molecular weight (M_n) was 88,877 Da, the weight average molecular weight (M_w) was 145,504 Da, and the polydispersity was 1.637. Therefore, the above results confirmed the successful synthesis of nano-SiO₂-modified fluorinated polyacrylate.

Table 1: Thermal stability of different silica content films

	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{\max}$ (°C)
AR-F	185.6	367.5	380.9
1% SiO ₂ @AR-F	186.1	373.5	386.8
2% SiO ₂ @AR-F	185.2	375.2	389.0
3% SiO ₂ @AR-F	186.3	376.1	389.1
4% SiO ₂ @AR-F	171.1	370.8	385.8

3.4 XPS analysis

The surface chemical elements of AR-F and SiO₂@AR-F were further characterized by XPS, as shown in Figure 5a. The binding energy at 687, 530, 283, and 99 eV corresponded to F 1s, O 1s, C 1s, and Si 2p, respectively (20). The AR-F spectrum had a peak at the binding energy of 687 eV, which proved that the fluoromonomer participated in the reaction. The sample with nano-SiO₂ added showed a Si 2p peak at the binding energy of 99 eV, which exhibited that the nano-SiO₂ participated in the polymerization reaction with acrylate. C–F (286.55 eV), C–F₃ (289.48 eV), and C–Si (282.54 eV) peaks also appeared in the C 1s (Figure 5b) spectrum. The XPS results were consistent with the previous study.

Figure 4: GPC curve of SiO₂@AR-F.

Figure 5: XPS scan spectra of AR-F and SiO₂@AR-F (a), C 1s (b), F 1s (c), and Si 2p (d) scan spectra of SiO₂@AR-F.

3.5 Hydrophobicity and film surface morphology (AFM) analysis

The surface hydrophobicity of the polymer films containing different amounts of SiO₂ was evaluated by measuring the water contact angle and water absorption rate, as shown in Figure 6. The surface hydrophobicity of the film was significantly promoted after SiO₂ was incorporated into fluorinated polyacrylate. With the increase of the SiO₂ content, the water absorption rate of the film decreased, and the water contact angle gradually increased. When 3% SiO₂ was added to the reaction, the water absorption rate reached the lowest (8.2%), and the water contact angle reached the highest (120°). At this time, the hydrophobic ability decreased when continuing to increase the content of SiO₂.

Figure 6: Comparative analysis of water absorption and contact angle.

The surface topography (AFM) of the adhesive film was further conducted to explore the reasons for the difference in the hydrophobicity of the film, and the results are shown in Figure 7, and the surface roughness is listed in Table 2. There were differences in surface roughness by comparing the three-dimensional (3D) images of the film with different SiO₂ contents. The surface of the AR-F sample without SiO₂ was relatively flat, and the 3D image had a little protrusion, which was mainly the part of the fluorine-containing segment enriched on the surface. The surface height map of AR-F had few peaks, average surface roughness was 1.92 nm, root mean square roughness (RMS) was 2.45 nm, and the surface roughness was the smallest, leading to the worst hydrophobicity. The surface roughness of the film gradually increased as the content of SiO₂ increased, showing more small bumps in the 3D images. When the addition amount of SiO₂ was 3%, the 3D map showed the smallest bumps, and the surface height map showed many and small peaks, and the hydrophobicity is better. Ra of 3% SiO₂@AR-F was 6.02 nm, and RMS was 7.63 nm, which exhibited the best hydrophobic properties. The film with 4% SiO₂ had the largest roughness, while the nano-SiO₂ agglomerated, and the peak shape of the surface height map was also relatively high and large, resulting in the decrease of the hydrophobic properties (22,23).

3.6 Corrosion resistance of the coating

3.6.1 Polarization curve (Tafel) analysis

Figure 8 shows the potential polarization curve of the coatings in the 3.5 wt% NaCl (aq). Table 3 lists the electrochemical parameters of E_{cor} (corrosion potential), i_{cor} (corrosion current density), and the corrosion inhibition efficiency (IE%). IE% was calculated by using Eq. 2 (24):

$$\text{IE\%} = \left(\frac{i_{\text{cor}}^0 - i_{\text{cor}}}{i_{\text{cor}}^0} \right) \times 100 \quad (2)$$

where the i_{cor}^0 and i_{cor} architectures represent the corrosion current density of bare boards and coated three-dimensional boards, respectively.

The higher the E_{cor} and the lower the i_{cor} of the coating are, the better the corrosion resistance of the coating is (25). The incorporation of SiO₂ effectively improved the corrosion resistance of the coating. E_{cor} of the AR-F coating without SiO₂ was -0.66371 V, which showed the highest corrosion current density ($1.48 \times 10^{-7} \text{ A}\cdot\text{cm}^{-2}$). In

contrast, the coatings containing SiO₂ exhibited a lower corrosion current density. Among them, the corrosion current density of the coating containing 3% SiO₂ was the lowest ($2.01 \times 10^{-9} \text{ A}\cdot\text{cm}^{-2}$), which indicated that the functionalized SiO₂-modified fluorinated acrylate coating effectively inhibited the reaction between the anode and the cathode of the metal substrate. The corrosion inhibition efficiency of the coatings with different SiO₂ contents increased from 85.2% to 99.8%, which was mainly due to the shielding effect of the nanoparticles on the corrosive medium.

3.6.2 Electrochemical impedance analysis

EIS is one of the most important and effective techniques for estimating the corrosion resistance of coatings. Therefore, EIS measurement was performed to further study the effects of the functionalized SiO₂-modified fluorinated polyacrylate polymer coating on the anticorrosion performance. The Bode and Nyquist plots obtained from the EIS data for different periods of time in the 3.5 wt% NaCl solution are shown in Figure 9. In general, the semicircle diameter of the Nyquist curve directly reflects the impedance value of the coating, indicating the shielding effect of the coating on the metal surface (26). The arc diameter of the AR-F coating without SiO₂ was the smallest regardless of the immersion time, and that of the coating with 3% SiO₂ was the largest, which showed that the shielding effect of nano-SiO₂ on the coating was significantly enhanced.

The low-frequency impedance in the Bode diagram is one of the important parameters of electrochemical tests, and the corrosion protection performance of the coating is easily compared between different systems (27). The higher the low-frequency impedance value is, the better the corrosion resistance of the coating is. The low-frequency impedance values of the coatings with different SiO₂ contents were significantly different after immersing in the 3.5 wt% NaCl solution for 1 day (Figure 8a). Among them, the AR-F coating without SiO₂ had the lowest low-frequency impedance value ($1.32 \times 10^5 \Omega\cdot\text{cm}^2$), and the fluorinated acrylate coating containing 3% SiO₂ had the highest low-frequency impedance value ($1.49 \times 10^7 \Omega\cdot\text{cm}^2$). With the extension of the immersion time, the low-frequency impedance value of the fluorinated acrylate coating with SiO₂ was always higher than that of the AR-F coating without SiO₂. The low-frequency impedance value of the 3% SiO₂@AR-F coating was always the largest, showing excellent corrosion resistance, which was due to the high surface roughness and the shielding effect of SiO₂ on the corrosive medium (28).

Figure 7: AFM diagrams, surface height diagrams, and 3D diagrams of different SiO_2 content: (a) 0% SiO_2 , (b) 1% SiO_2 , (c) 2% SiO_2 , (d) 3% SiO_2 , and (e) 4% SiO_2 .

Table 2: Surface height map of different SiO₂ content adhesive films

Sample	AR-F	1% SiO ₂ @AR-F	2% SiO ₂ @AR-F	3% SiO ₂ @AR-F	4% SiO ₂ @AR-F
Ra (nm)	1.92	3.13	4.0	6.02	6.91
RMS (nm)	2.45	4.24	5.39	7.63	8.94

Ra, average surface roughness (21).

Figure 8: Polarization curve of potential dynamics.

3.6.3 SEM analysis of corrosion area and salt spray resistance test

The corrosion area of the substrates after the peeling off the coatings immersed in the 3.5 wt% NaCl solution for 9 days was observed by SEM to further confirm the electrochemical test results, as shown in Figure 10. The surface of the tinplate protected by the AR-F coating without SiO₂ (Figure 10a) suffered severe corrosion with large and deep corrosion areas. The surface of the tinplate protected by the modified fluorinated acrylate coating with the addition of 3% SiO₂ (Figure 10b) had very little corrosion, and the corrosion area was small and shallow. These phenomena indicated that the incorporation of nano-SiO₂ significantly improved the corrosion

resistance of the fluorinated acrylate coating, which was consistent with the above electrochemical analysis.

The salt spray tests evaluate the corrosion resistance of the coating by simulating environmental conditions with a salt spray tester (29). The salt spray machine was used to test the salt spray resistance of the coating after 24, 120, and 216 h, and the test results are shown in Figure 11. The corrosion degree of the AR-F coating without SiO₂ was greater at the scratches with the immersion time, while the coating added with nano-SiO₂ had little corrosion and change at the scratches, which indicated that the corrosion resistance of the nano-SiO₂-modified fluorinated acrylate was higher than that of the pure fluorinated acrylate. Nano-SiO₂-modified fluorinated acrylate enhanced the hydrophobicity of the coating, reduced the internal gap of the coating, and effectively prevented the intrusion of the corrosive medium.

3.7 Analysis of coating physical properties

Table 4 lists the results of the pencil hardness, impact resistance, adhesion, and heat resistance of the coating measured according to various national standards. The coatings with different SiO₂ contents had various physical properties. The pencil hardness without SiO₂ coating (AR-F) was H, the impact resistance was greater than 30 cm, the adhesion level was 4, and the heat resistance was poor (crack at high temperature), which shows the poor physical properties of the coating. The incorporation of functionalized SiO₂ improved the physical properties of the coatings, and the 3% SiO₂@AR-F coating had the best performance. The pencil hardness of the 3% SiO₂@AR-F coating was 3H, the impact resistance was greater than 50 cm, the adhesion level was 2, and the heat resistance was good. However, the fluorine-containing segments were difficult to migrate to the surface of the coatings after adding extensive SiO₂, which led to the agglomeration of SiO₂, thus reducing the physical properties of the coatings. Therefore, the performance of the coating with 3% SiO₂ was the best.

Table 3: Electrochemical parameters of coatings with different SiO₂ contents immersed in 3.5 wt% NaCl solution

Sample	AR-F	1% SiO ₂ @AR-F	2% SiO ₂ @AR-F	3% SiO ₂ @AR-F	4% SiO ₂ @AR-F
E_{corr} (V)	-0.66371	-0.46803	-0.20089	-0.12820	-0.17328
i_{corr} (A·cm ⁻²)	1.48×10^{-7}	1.58×10^{-8}	5.32×10^{-9}	2.01×10^{-9}	3.97×10^{-9}
IE (%)	85.20	98.42	99.47	99.80	99.60

Figure 9: Bode (a–e) graph and Nyquist (a'–e') graph of coating under different immersion time: 1 (a, a'), 3 (b, b'), 5 (c, c'), 7 (d, d'), and 9 days (e, e').

Figure 10: SEM image of peeling tinplate surface after 9 day immersion in 3.5 wt% NaCl solution: (a) AR-F and (b) 3% SiO₂@AR-F.

Figure 11: Salt spray test diagrams at different times: (a) AR-F, (b) 1% SiO₂@AR-F, (c) 2% SiO₂@AR-F, (d) 3% SiO₂@AR-F, and (e) 4% SiO₂@AR-F.

3.8 Corrosion protection mechanism

The corrosion protection mechanism of the coatings is shown in Figure 12. In general, during the coating curing process, some micropores were formed on the metal surface under the evaporation of the solvent. At the same

time, the hydrophilic component of the coatings formed some water channels, and the corrosive medium easily penetrated the coating to reach the metal substrate (30,31). SiO₂ nanoparticles had the characteristics of high specific surface area and large surface curvature, which adsorbed more resins on their surface, reduced the free volume

Table 4: Physical properties of coatings with different SiO₂ contents

Sample	Pencil hardness (level)	Impact resistance (cm)	Adhesion (level)	Heat resistance (150°C)
AR-F	H	≥30	4	Cracked, yellowed
1% SiO ₂ @AR-F	H	≥50	3	No change
2% SiO ₂ @AR-F	2H	≥50	2	No change
3% SiO ₂ @AR-F	3H	≥50	2	No change
4% SiO ₂ @AR-F	H	≥50	3	No change

Figure 12: Corrosion protection mechanism.

of the coating, formed nanocomposite coatings, increased the crosslinking density of the coating, thus preventing the corrosive substances from entering the substrate. The uniformly distributed nano-SiO₂-modified fluorinated acrylate increased the tortuosity of the corrosion electrolyte diffusion path (Figure 12). The dispersion state of nano-SiO₂ in the polymer matrix played an important role in improving its anticorrosion performance, compatibility, and interaction.

4 Conclusion

In this experiment, KH-570 was used to modify the surface of nano-SiO₂ and by introducing reactive functional groups to obtain functionalized nano-SiO₂. The functionalized SiO₂@AR-F was prepared by initiating free radical polymerization with a dual initiator. The results of FTIR, ¹H-NMR, and XPS fully proved that the graft polymerization of acrylate monomers on the surface of nano-SiO₂ was completed. The obtained waterborne coating had excellent hydrophobic properties and corrosion resistance, the contact angle reached 120°, and the electrochemical impedance value reached $1.49 \times 10^7 \Omega \cdot \text{cm}^2$. The coating with nano-SiO₂ showed excellent pencil hardness, adhesion, and other physical properties. The introduction of fluorine-containing groups in the coating effectively reduced the surface energy. The nano-SiO₂ filled the gaps of the coating, increased the surface roughness, prevented the corrosive medium from entering the inside of the substrate, and effectively improved the anticorrosion ability of the coating. The waterborne hydrophobic anticorrosive coating was expected to become a functional coating with broad application prospects.

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