

Review

Facile fabrication of BTA-SiO₂@Al₂O₃ core-shell microspheres for simultaneously enhanced anticorrosion, thermal and mechanical properties of waterborne epoxy coatings

Qiang Lei^a, Xinyu Wang^b, Zhiguo Xiong^b, Runqi Ruan^c, Xiao Wang^c, Rulin Li^a, Yilin Jiang^a, Dongpeng Wang^a, Weilong Shi^a, Weili Li^{a,*}

^a School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003, China

^b China Ship Development and Design Center, Wuhan, 430064, China

^c State Key Laboratory of Coatings for Advanced Equipment, Marine Chemical Research Institute Co., Ltd., Qingdao, 266071, China

ARTICLE INFO

Keywords:

Waterborne epoxy coatings
SiO₂@Al₂O₃ core-shell microspheres
Benzotriazole (BTA)
Anticorrosion performance
Synergistic protection mechanism

ABSTRACT

Waterborne epoxy (WEP) coatings have attracted extensive attention in the field of anticorrosion due to their environmental friendliness, low toxicity, and excellent adhesion. However, the inherent defects such as high porosity, poor thermal stability, and insufficient long-term corrosion resistance severely limit their practical applications in harsh marine environments. Herein, a novel benzotriazole BTA-SiO₂@Al₂O₃ core-shell composite filler was designed and synthesized, which integrates the physical barrier effect of inorganic microspheres and the active corrosion inhibition function of BTA. A series of BTA-SiO₂@Al₂O₃-WEP composite coatings with filler loadings ranging from 5 to 25 wt% were prepared, and their thermal stability, mechanical properties, and anticorrosion performance were systematically investigated. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results showed that the introduction of core-shell fillers significantly improved the thermal stability and glass transition temperature (*T*_g) of WEP coatings. The initial decomposition temperature (5% mass loss temperature) of the composite coating with 25 wt% filler loading reached 295.04 °C, which was 101.79 °C higher than that of neat WEP. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests demonstrated that the composite coating with 20 wt% filler loading exhibited the optimal anticorrosion performance, with a corrosion rate approximately two orders of magnitude lower than that of neat WEP coating. The 240 h neutral salt spray test further confirmed its excellent long-term protective performance, with only negligible corrosion products observed at the artificial scratch, indicating favorable active corrosion protection capability at coating defects. X-ray photoelectron spectroscopy (XPS) analysis revealed that BTA molecules could be released with the penetration of corrosive media and form a dense Fe-BTA chelated passivation film on the steel substrate surface through coordination bonds. This work provides a facile and effective strategy for the fabrication of high-performance waterborne epoxy anticorrosion coatings, which have promising applications in marine engineering and industrial protection fields.

1. Introduction

Waterborne epoxy resins (WEP) combine the excellent adhesion, chemical resistance, mechanical strength, and film-forming properties of epoxy resins with low volatile organic compound (VOC) content, environmental friendliness, and high construction safety due to their aqueous dispersion medium. Consequently, they have gained widespread applications in anticorrosive coatings, industrial protection, building materials, adhesives, and composite functional materials. With

increasing global green manufacturing and low-carbon requirements, waterborne epoxy systems are gradually replacing traditional solvent-based epoxies as the mainstream in protective coatings [1]. However, compared with solvent-based counterparts, waterborne epoxies are susceptible to uneven water evaporation, incomplete emulsion particle fusion, and phase separation during curing, inevitably forming micropores, interfacial defects, or local stress concentration within the coating [2]. Additionally, they exhibit inherent drawbacks including relatively low crosslinking density, high brittleness, insufficient wear resistance,

* Corresponding author.

E-mail address: liweili@just.edu.cn (W. Li).

<https://doi.org/10.1016/j.porgcoat.2026.110454>

Received 13 June 2026; Received in revised form 13 July 2026; Accepted 17 July 2026

0300-9440/© 2026 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

and limited anticorrosion performance, which severely restrict their large-scale application in high-performance protection and structural-functional integration field [3]. Therefore, improving the comprehensive properties of waterborne epoxies through filler composite modification has become a core research direction. Among various strategies, multi-component composite filler synergistic modification has attracted extensive attention from academia and industry for its ability to simultaneously enhance multiple key coating properties [4,5].

Inorganic filler incorporation is one of the most effective approaches to improve the mechanical properties, wear resistance, thermal stability, and barrier properties of epoxy resins. Various fillers such as graphene [6,7], carbon nanotubes [8,9], boron particles [10], silica [11,12], and clay [13] have been widely investigated for epoxy composite modification. Kosedag et al. [14] compared the effects of graphene and silicon carbide (SiC) nanoparticles on carbon fiber-reinforced composites, finding graphene more effective in enhancing tensile and flexural strength. Shishevan et al. [15] reported that graphene nanoplates significantly improved the low-velocity impact performance and energy absorption capacity of basalt fiber-reinforced epoxy composites. Recently, two-dimensional hexagonal boron nitride (h-BN)-based composites have emerged as a research hotspot due to their exceptional thermal conductivity, chemical stability, and electrical insulation. Lu et al. [16] developed a urushiol-based biomimetic coating by sol-gel coating of SiO_2 on h-BN, followed by 3-(methacryloyloxy) propyltrimethoxysilane (MPS) functionalization and natural urushiol (Ur) grafting. The resulting hydrophobic, highly dispersed hybrid fillers, when incorporated into WEP at optimal loading, yielded coatings with excellent thermal and mechanical properties, maintaining a low-frequency impedance modulus of $2.33 \times 10^{10} \Omega \cdot \text{cm}^2$ after 270 h immersion in 3.5 wt% NaCl solution. Physically modified boron nitride fillers have also been shown to enhance functional coating performance [17], while advanced biomimetic lacquer alcohol-modified SiO_2 @BN hybrids simultaneously improved both thermal conductivity and corrosion resistance through optimized interfacial structures [18]. Multidimensional filler systems, leveraging synergistic effects between components of different dimensions, represent an important trend in epoxy modification. For instance, epoxy polysiloxane- SiO_2 nanoparticle coatings achieved excellent wear resistance, hydrophobicity, and antifouling properties through surface engineering [19].

Among inorganic fillers, alumina (Al_2O_3) is widely used for polymer composite reinforcement due to its high hardness, thermal stability, chemical inertness, and good thermal conductivity [20–22]. Numerous studies demonstrate that Al_2O_3 significantly improves the mechanical strength, wear resistance, and heat resistance of epoxy coatings [23]. For example, $\gamma\text{-Al}_2\text{O}_3$ modified with titanate coupling agents enhanced the mechanical, thermal, and corrosion resistance properties of epoxy coatings by improving interfacial compatibility and bonding strength between fillers and matrix [24]. Silica sol, an inorganic colloid containing abundant nano- SiO_2 particles and active silanol groups, forms hydrogen bonds or undergoes condensation reactions with hydroxyl groups on alumina surfaces, improving filler dispersion in aqueous epoxy system. Furthermore, nano-silica from silica sol participates in constructing denser inorganic-organic composite networks during curing, effectively filling micropores and prolonging diffusion paths for corrosive media, oxygen, and water molecules, thereby enhancing barrier performance [25].

Benzotriazole (BTA), a classic nitrogen-containing heterocyclic corrosion inhibitor, forms dense adsorption films and stable coordination compounds on metal surfaces through its multiple coordinating nitrogen atoms [26]. Beyond corrosion inhibition, BTA improves filler organic affinity and enhances interfacial interactions with epoxy matrices via hydrogen bonding, coordination, and molecular adsorption. Recent advances in BTA-based composite systems include BTA-doped epoxy coatings with passive synergistic protection, mixed $\text{Zn}_3(\text{PO}_4)_2$ -BTA@ SiO_2 systems combining SiO_2 barrier effects with synergistic anodic/cathodic inhibition [27], and dual-responsive

Fe_3O_4 @BTA-ZIF-8 nanocontainers enabling magnetic field-oriented distribution and pH-controlled release [28]. Spherical ZP-based pigments prepared by double cation co-precipitation also demonstrated improved dispersion and sustained-release properties, extending coating service life [29]. Compared with single filler modification, BTA incorporation enables the construction of composite systems integrating inorganic reinforcement, nano-filling, and organic interface regulation, maximizing synergistic enhancement effects [30].

Based on the above analysis, this study innovatively designed a ternary composite filler system composed of spherical Al_2O_3 , silica sol-derived SiO_2 , and BTA for waterborne epoxy modification. We systematically investigated the effects of this composite filler on the mechanical properties, wear resistance, thermal stability, and corrosion resistance of WEP, along with the underlying mechanisms. In this system, spherical alumina provides rigid reinforcement, wear resistance, and thermal stability; silica sol improves filler dispersion, enhances interfacial transition layers, and increases coating density; while BTA exerts corrosion inhibition and further strengthens filler-matrix interactions through molecular-level adsorption and coordination. The synergistic effects of these three components are expected to comprehensively improve the performance and long-term service reliability of waterborne epoxy coatings. This work provides a simple, feasible strategy for high-performance and functional modification of waterborne epoxies, offering theoretical and experimental support for their application in harsh environments such as marine engineering and petrochemical industries.

2. Experimental section

2.1. Materials

Spherical $\alpha\text{-Al}_2\text{O}_3$ microspheres with an average particle size of 10 μm were supplied by Denka Company Limited (Japan). Alkaline aqueous silica sol (25 wt% SiO_2) was purchased from Nissan Chemical Corporation (Japan). Benzotriazole (BTA, $\geq 99\%$) was obtained from Sigma-Aldrich (Merck KGaA, Germany). Waterborne epoxy dispersion (WEP, EPIKOTE™ 3515-W-60 A) was used as the polymeric matrix, which was provided by Hexion Inc. (USA); the typical properties are solid content of 60 wt%, epoxy equivalent weight (EEW) of 450–550 g/eq, viscosity of 500–3000 mPa·s at 25 °C, and pH of 6.5–8.5. Waterborne polyamide curing agent AQUAEP0-3132 was provided by Huntsman Corporation (USA). Propylene glycol methyl ether (PM, analytical grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Wetting and dispersing agent BYK-2601 was purchased from BYK-Chemie GmbH (Germany). Butyl acetate and anhydrous ethanol (analytical grade) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was prepared in our laboratory.

2.2. Preparation of SiO_2 @ Al_2O_3 composite microspheres

At first, PM and deionized water were mixed at a volume ratio of 1:1 under magnetic stirring for 10 min to construct a homogeneous cosolvent system. PM was employed as a cosolvent to lower the excessively high surface tension of water, which significantly enhanced the wettability of silica sol onto the high-surface-energy $\alpha\text{-Al}_2\text{O}_3$ microspheres and facilitated the uniform spreading of silica sol on the particle surface. Subsequently, $\alpha\text{-Al}_2\text{O}_3$ microspheres and aqueous silica sol were added sequentially at a mass ratio of 1:4, followed by the introduction of 0.5 wt % BYK-2601 wetting dispersant relative to the total solid content. The suspension was ultrasonicated for 60 min at room temperature and further mechanically stirred at 1000 rpm for 60 min to ensure the uniform adsorption and coating of SiO_2 onto Al_2O_3 . The mixture was concentrated via rotary evaporation at 45–50 °C under reduced pressure. The obtained wet powder was dried at 80 °C for 12 h, gently ground in an agate mortar, and sieved through a 200-mesh screen to yield dry SiO_2 @ Al_2O_3 composite microspheres.

2.3. Preparation of BTA-SiO₂@Al₂O₃ composite microspheres

The mass ratio of Al₂O₃ to SiO₂ in the obtained core-shell carrier was approximately 1:4, consistent with the feeding ratio of alumina sol to silica sol. BTA was dissolved in butyl acetate to prepare a 5 wt% BTA solution. BTA exhibits strong adsorption affinity toward the silica sol shell due to abundant silanol groups (Si-OH) on the surface of SiO₂@Al₂O₃ microspheres. Polar N-containing groups in BTA molecules can form hydrogen bonds with Si-OH groups, enabling stable and uniform adsorption of BTA onto the SiO₂ surface without obvious desorption. SiO₂@Al₂O₃ microspheres were immersed in the BTA solution and stirred at room temperature for 2 h to allow sufficient adsorption of BTA. The solid was collected by vacuum filtration, washed twice with butyl acetate, and dried at 60 °C under vacuum for 6 h to remove residual solvent, yielding BTA-loaded BTA-SiO₂@Al₂O₃ composite microspheres.

2.4. Preparation of BTA-SiO₂@Al₂O₃-WEP composite coatings

BTA-SiO₂@Al₂O₃ composite microspheres were incorporated into WEP (EPIKOTE™ 3515-W-60 A) at filler loadings of 5, 10, 15, 20, and 25 wt%, denoted as BTA-SiO₂@Al₂O₃-WEP-X (X = 5, 10, 15, 20, 25). The filler loading (5–25 wt%) is defined as the total mass of the BTA-SiO₂@Al₂O₃ composite filler (including loaded BTA) relative to the mass of the waterborne epoxy resin matrix. The mixture was ball-milled at 1500 rpm for 120 min to achieve uniform dispersion.

Q235 carbon steel substrates and glass slides were polished with 400#, 800#, and 1200# SiC sandpapers sequentially, ultrasonically cleaned with anhydrous ethanol for 10 min, and dried in cold air. WEP and waterborne curing agent were mixed at a mass ratio of 2:1. The mixture was coated onto substrates using a bar coater to achieve a dry film thickness of approximately 90 ± 5 μm. All coatings were cured at room temperature for 24 h and post-cured at 60 °C for 2 h to enhance

crosslinking and compactness.

Fig. 1 schematically illustrates the preparation routes of BTA-SiO₂@Al₂O₃ composite microspheres and the corresponding composite coatings. Fig. 1a shows the fabrication of BTA-SiO₂@Al₂O₃ core-shell structures and subsequent BTA adsorption via hydrogen bonding between BTA and surface Si-OH groups. Fig. 1b displays the blending of BTA-SiO₂@Al₂O₃ with waterborne epoxy dispersion (WEP), coating, and curing processes to form the final composite anticorrosion coatings.

2.5. Characterization

Fourier transform infrared (FTIR) spectroscopy was employed to characterize the chemical structures and functional groups of raw materials and as-prepared composite microspheres. Field emission scanning electron microscopy (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to observe the surface morphologies of BTA-SiO₂@Al₂O₃ composite fillers and the cross-sectional morphologies of composite coatings as well as the corresponding elemental distribution. X-ray diffraction (XRD) was applied to analyze the phase compositions and crystal structures of pristine α-Al₂O₃ and BTA-SiO₂@Al₂O₃ composite fillers with Cu K_α radiation (λ = 0.15418 nm) over a 2θ range of 10° to 90° at an accelerating voltage of 40 keV. UV-Vis absorption spectroscopy (Shimadzu UV-2600, Japan) was used to quantify the BTA loading and investigate the pH-responsive release behavior of BTA-SiO₂@Al₂O₃ fillers. First, BTA standard solutions with concentrations of 1, 5, and 10 mg/L were prepared at pH = 4, 7, and 10, respectively, and their absorbance at the characteristic absorption wavelength was measured to establish standard calibration curves. For the release test, a certain amount of BTA-SiO₂@Al₂O₃ filler was dispersed in 3.5 wt% NaCl solution with different pH values, and the supernatant was collected at preset time intervals for UV-Vis detection. The BTA loading was determined by the total release amount after 210 min of stirring at pH =

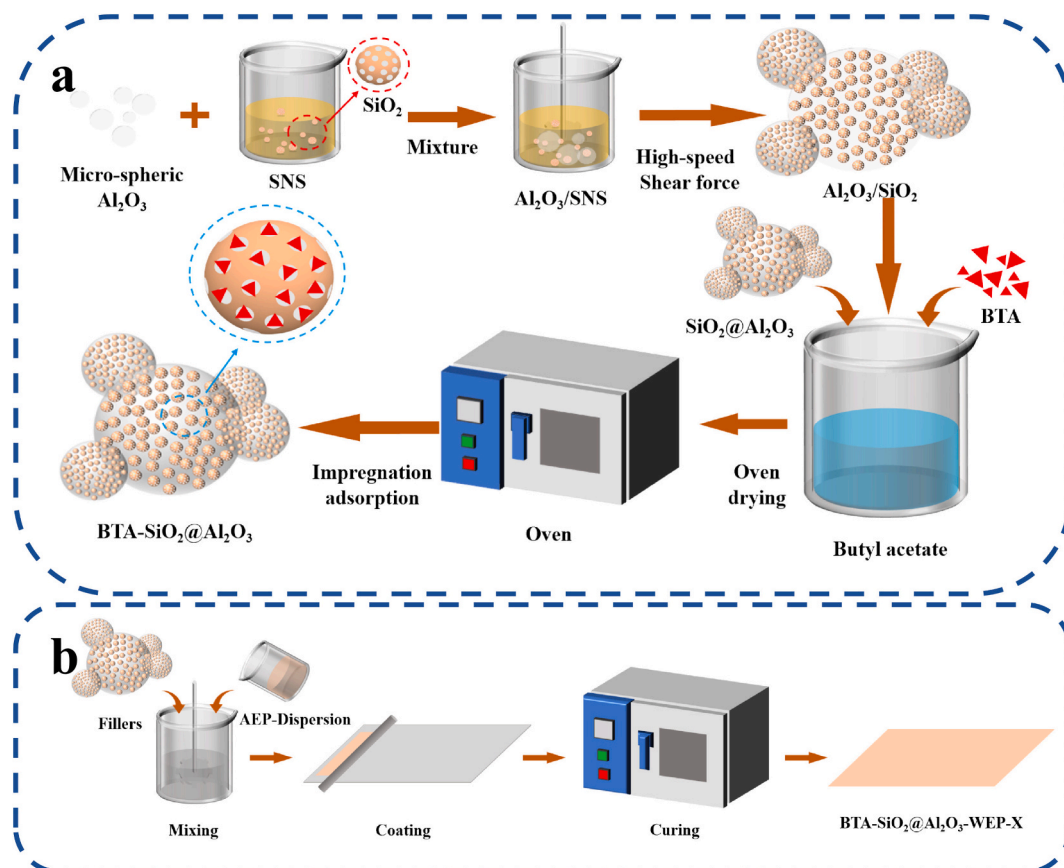


Fig. 1. Schematic Diagram of the Preparation Process for (a) BTA-SiO₂@Al₂O₃ and (b) BTA-SiO₂@Al₂O₃-WEP-X coating.

4, under which condition BTA was completely released from the carriers. Laser scanning confocal microscopy (LSCM) was utilized to characterize the three-dimensional surface morphology and roughness of cured composite coatings. Differential scanning calorimetry (DSC) was carried out on a NETZSCH DSC 214 instrument to determine the glass transition temperature and thermal dynamic properties of cured coatings, while thermogravimetric analysis (TGA) was performed on a Diamond TG-DTA analyzer to evaluate their thermal stability. Pencil hardness, flexibility, impact resistance, and adhesion strength were measured in accordance with corresponding national standards using a BGD 506/1 pencil hardness tester, QTX paint film elasticity tester, BGD 302 tubular film impactor, and BGD 500 digital coating adhesion tester, respectively. Abrasion resistance was evaluated using a BGD 523 paint film abrasion tester following GB/T 1768–2008 with a 500 g load and 450 rotation cycles. Corrosion resistance was evaluated by electrochemical impedance spectroscopy (EIS) and Tafel polarization curves on a CS2350H electrochemical workstation in 3.5 wt% NaCl solution using a three-electrode system; Tafel curves were recorded at 2.5 mV/s within ± 0.25 V vs. open circuit potential (OCP), and EIS tests were conducted from 100 kHz to 0.01 Hz with a 10 mV AC amplitude [31]. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface elemental composition and chemical valence states of corroded steel substrates. To further verify the reliability of the electrochemical test results and evaluate the practical protective performance of the coatings in a simulated marine atmospheric environment, a 240 h neutral salt spray accelerated corrosion test was conducted on the neat WEP coating and BTA-SiO₂@Al₂O₃-WEP composite coatings with different filler loadings. All specimens were prepared with standardized artificial scratches (2.0 cm length, 0.5 mm width, through-coating to substrate) and tested under the conditions specified in GB/T 10125–2012.

3. Results and discussion

3.1. Structural and morphological characterization of BTA-SiO₂@Al₂O₃ composite microspheres and their intermediates

Firstly, the structure, morphology, and physicochemical properties of the as-prepared BTA-SiO₂@Al₂O₃ were systematically characterized via FTIR spectroscopy, XRD, and FESEM respectively.

FTIR spectroscopy was utilized to characterize the chemical structures and functional groups of pure BTA, α -Al₂O₃, amorphous SiO₂, SiO₂@Al₂O₃ core-shell microspheres, and BTA-SiO₂@Al₂O₃ composite microspheres [32]. The retention, emergence, and regular shift of characteristic absorption peaks provide conclusive evidence for the effective core-shell hybridization of SiO₂ onto α -Al₂O₃ and the stable adsorption of BTA onto the composite fillers. Pure α -Al₂O₃ microspheres present strong characteristic absorption peaks at 560 cm⁻¹ and 720 cm⁻¹ assigned to the stretching vibrations of Al—O bonds, which are typical FTIR signals of the α -Al₂O₃ corundum phase; pure alkaline silica sol exhibits a prominent absorption peak at 1160 cm⁻¹ for the asymmetric stretching vibration of Si—O—Si bonds, a characteristic peak at 847 cm⁻¹ for the bending vibration of Si—O bonds, and broad absorption bands at $\sim$ 3400 cm⁻¹ and 1630 cm⁻¹ corresponding to the O—H stretching and bending vibrations of surface silanol (Si—OH) groups, respectively. For SiO₂@Al₂O₃ composite microspheres, the characteristic Al—O peaks of α -Al₂O₃ are fully preserved, confirming that the sol-gel coating process does not destroy the intrinsic crystal structure of the α -Al₂O₃ core, while all characteristic absorption peaks of amorphous SiO₂ are newly detected, directly verifying the successful and stable coating of amorphous SiO₂ on α -Al₂O₃ microspheres to form a well-defined core-shell structure. Pure BTA shows distinctive characteristic peaks, including weak absorption at 3000–3100 cm⁻¹ for the C—H stretching of the benzene ring, a peak near 3200 cm⁻¹ for the N—H stretching of the triazole ring, strong peaks at 1400–1600 cm⁻¹ for the skeletal stretching of C=C and C=N bonds in aromatic and triazole rings, and peaks at 1200–1300 cm⁻¹ for the stretching of C—N and N—N

bonds in the triazole ring; in the spectrum of BTA-SiO₂@Al₂O₃, all core characteristic peaks of the SiO₂@Al₂O₃ core-shell structure are retained, indicating that BTA adsorption does not damage the framework of the composite microspheres, and all characteristic peaks of BTA are clearly observed, confirming the successful introduction of BTA into the composite system. Notably, the broad Si—OH absorption band near 3400 cm⁻¹ in BTA-SiO₂@Al₂O₃ displays an obvious red shift and peak broadening compared with that of SiO₂@Al₂O₃, which originates from the formation of strong intermolecular hydrogen bonds between the electron-rich N atoms in the BTA triazole ring and the hydroxyl hydrogen atoms in the surface Si—OH groups of the SiO₂ shell, demonstrating that BTA is stably and uniformly adsorbed onto the SiO₂ shell via hydrogen bonding instead of simple physical mixing or residual solvent, which is consistent with the homogeneous distribution of N element in the EDS elemental maps. These FTIR results furnish critical structural and functional group support for the improved physical barrier and corrosion inhibition properties of the subsequent composite coatings.

Fig. 2(b) shows the XRD patterns of pristine α -Al₂O₃ and as-synthesized BTA-SiO₂@Al₂O₃ core-shell microspheres. Both samples exhibit well-defined, sharp diffraction peaks at $2\theta = 25.6^\circ, 35.1^\circ, 43.4^\circ, 52.6^\circ, 57.5^\circ, 66.5^\circ, \text{ and } 68.2^\circ$, all assigned to the characteristic reflections of the corundum phase of α -Al₂O₃. The full retention of the peak profile for BTA-SiO₂@Al₂O₃ confirms that the sol-gel SiO₂ coating process does not alter the intrinsic crystalline structure of the α -Al₂O₃ core. A slight decrease in the intensity of these characteristic peaks is observed for the composite microspheres relative to bare α -Al₂O₃, attributed to the X-ray shielding and scattering effects of the amorphous SiO₂ shell. Concurrently, a distinct broad diffraction hump in the 2θ range of 17.5° – 22° provides direct evidence for the successful deposition of amorphous SiO₂ onto the α -Al₂O₃ surface. No characteristic diffraction peaks of BTA are detected in the pattern, which is rationalized by the low loading of BTA on the composite fillers, whose weak diffraction signals are completely obscured by the dominant signals from the Al₂O₃ core and SiO₂ shell.

Fig. 2(c) shows the surface morphology and elemental composition of as-synthesized BTA-SiO₂@Al₂O₃ core-shell microspheres, characterized by FESEM with EDS. In contrast to the smooth surface of pristine α -Al₂O₃ microspheres, the BTA-SiO₂@Al₂O₃ composite fillers display a rough yet uniform surface texture, arising from a dense, conformal amorphous SiO₂ shell tightly anchored onto the α -Al₂O₃ microsphere core. The homogeneous distribution of the silica component with consistent particle size confirms that the sol-gel coating and drying process were precisely regulated, eliminating particle agglomeration, shell cracking, and inhomogeneous deposition.

The water/PM cosolvent system plays a critical role in forming this high-quality SiO₂ shell: it modulates the hydrolysis–condensation kinetics of the silica sol, suppresses premature gelation during high-speed dispersion and ultrasonication, and mitigates shell shrinkage/cracking during drying, thus enabling the growth of a continuous, defect-free SiO₂ layer. The abundant surface Si—OH groups of the SiO₂ shell further serve as hydrogen-bonding sites to enable stable, uniform adsorption of BTA molecules onto the microsphere surface. Beyond enabling BTA immobilization, this core-shell architecture effectively mitigates the inherent self-aggregation of inorganic microfillers in the WEP matrix, which is critical for improving the processability and structural uniformity of the final composite coatings.

The corresponding EDS elemental maps reveal homogeneous spatial distribution of Si, O, and N throughout individual BTA-SiO₂@Al₂O₃ microspheres. This uniform elemental dispersion unambiguously verifies the successful conformal coating of SiO₂ and efficient loading of BTA without detectable phase segregation. Taken together, the FESEM and EDS results validate the rational design and successful fabrication of BTA-SiO₂@Al₂O₃ core-shell microspheres with a well-defined architecture, uniform composition, and favorable interfacial properties, making them promising functional fillers for high-performance

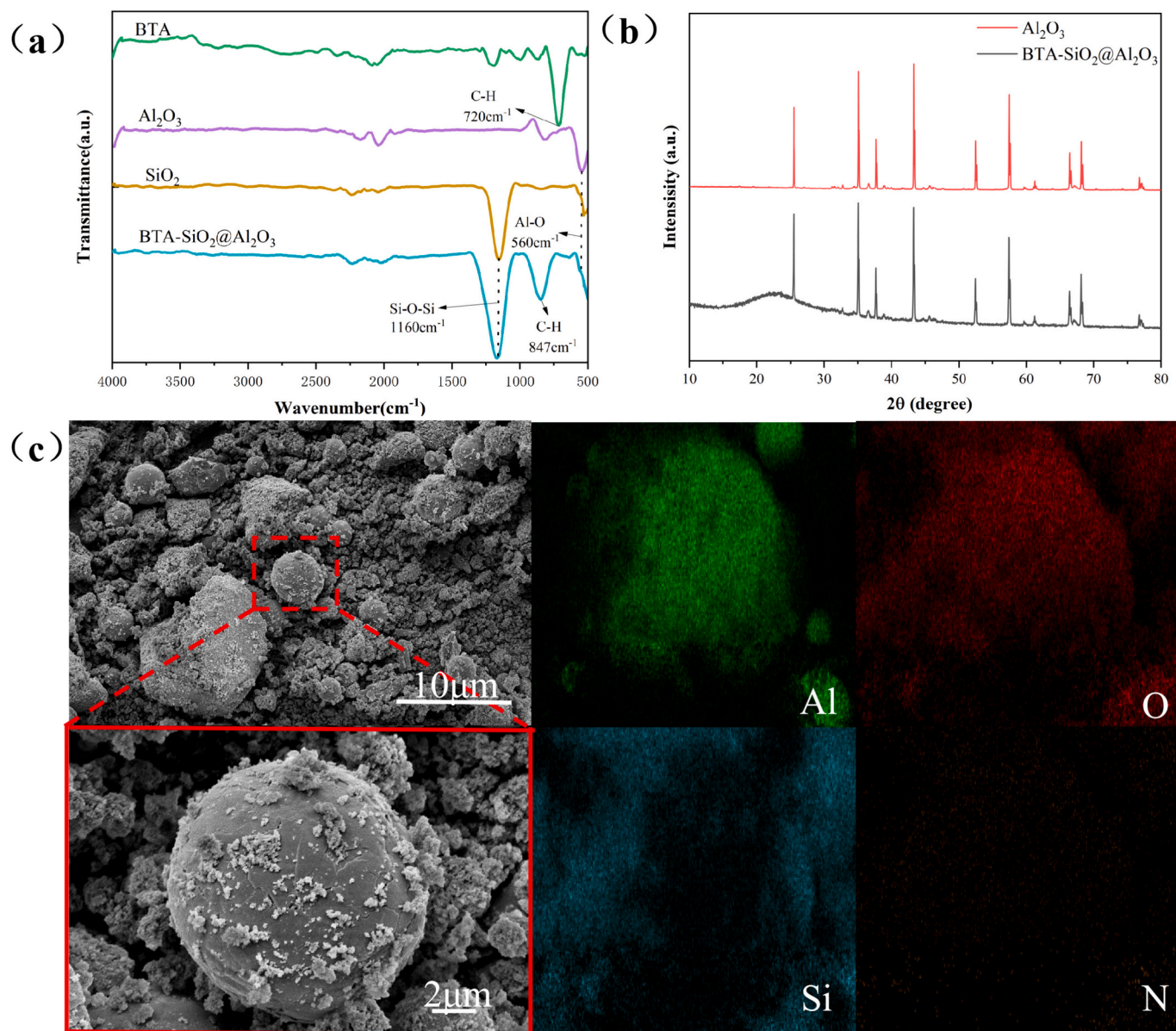


Fig. 2. (a) FTIR spectra of BTA, pristine α -Al₂O₃, amorphous SiO₂, and BTA-SiO₂@Al₂O₃ composite microspheres; (b) XRD patterns of pristine α -Al₂O₃ and BTA-SiO₂@Al₂O₃ microspheres; (c) FESEM image and corresponding EDS analysis of BTA-SiO₂@Al₂O₃ composite microspheres.

anticorrosion coatings.

3.2. pH-responsive release behavior of BTA

To elucidate the active protection mechanism of the BTA-SiO₂@Al₂O₃ /WEP coating, the release behavior of BTA from the core-shell nanocarriers under different pH conditions was systematically investigated via UV-Vis absorption spectroscopy.

First, the UV-Vis spectrum of the pristine SiO₂@Al₂O₃ carrier was tested to eliminate its spectral interference on BTA quantitative detection (Fig. 3a). No obvious characteristic absorption peak appeared in the wavelength range of 200–800 nm, confirming that the inorganic carrier itself does not affect the accuracy of BTA concentration measurement. Subsequently, BTA standard solutions with gradient concentrations (1, 5, 10 mg/L) were prepared at pH = 4, 7, and 10 respectively, and their absorption spectra are shown in Fig. 3b-d. The maximum characteristic absorption peaks of BTA were located at 260 nm, 250 nm, and 260 nm under acidic, neutral, and alkaline conditions, respectively. The linear fitting curves of absorbance versus BTA concentration at the three pH

values all show good linear correlation (Fig. 3e), which can be used for subsequent quantitative calculation of BTA concentration.

The time-resolved UV-Vis absorption spectra of BTA released from BTA-SiO₂@Al₂O₃ fillers in 3.5 wt% NaCl solution at different pH values are presented in Fig. 3f-h. The cumulative release percentages of BTA calculated from the standard curves are plotted in Fig. 3i. The whole release process can be divided into three stages: the rapid release stage within the first 60 min, the medium-speed release stage from 60 to 150 min, and the slow release stage from 150 to 210 min. The release rate follows the order of pH = 4 > pH = 10 > pH = 7, showing a significant pH-dependent controlled release behavior.

The underlying mechanism of the pH-responsive release can be explained as follows: under strong acidic conditions, H⁺ can hydrolyze and destroy the outer SiO₂ barrier layer and dissolve the inner Al₂O₃ carrier; meanwhile, the protonation of BTA molecules weakens the interfacial adsorption force between BTA and the carrier. The triple effects jointly promote the rapid and massive release of BTA. Under neutral conditions, the dense SiO₂ shell seals the pore channels of the carrier, and the inorganic framework remains stable, so only a small

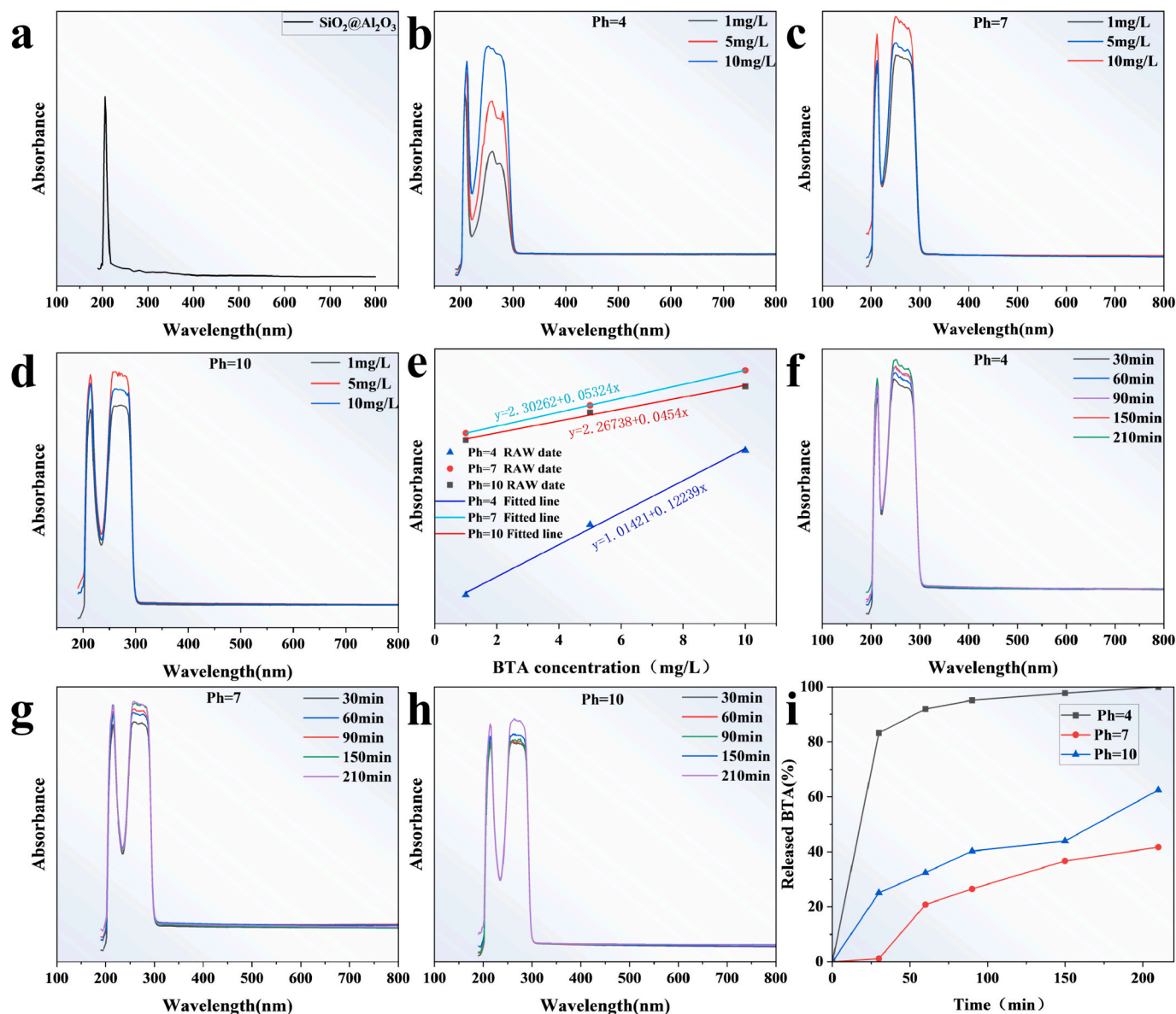


Fig. 3. UV-Vis characterization of pH-responsive BTA release behavior of BTA-SiO₂@Al₂O₃ fillers. (a) UV-Vis absorption spectrum of pristine SiO₂@Al₂O₃ carrier; (b-d) UV-Vis absorption curves of BTA standard solutions with different concentrations at pH = 4, 7, and 10; (e) Fitted standard curves of absorbance versus BTA concentration under three pH conditions; (f-h) UV-Vis absorption spectra of released BTA from BTA-SiO₂@Al₂O₃ at different immersion time at pH = 4, 7, and 10; (i) Cumulative BTA release percentage within 210 min under different pH conditions.

amount of BTA is released slowly. Under alkaline conditions, OH⁻ causes slight etching of the silica framework, resulting in a moderate release rate between acidic and neutral conditions.

Notably, after stirring for 210 min in pH = 4 3.5 wt% NaCl solution, BTA was almost completely released from the BTA-SiO₂@Al₂O₃ nanoparticles. Therefore, the total BTA content released under this condition was defined as the BTA loading capacity of the composite filler. Based on the standard curve calculation, the BTA loading was approximately 5 wt % relative to the total mass of the BTA-SiO₂@Al₂O₃ composite filler. This pH-responsive on-demand release behavior endows the coating with active anticorrosion capability: when local acidification occurs at coating defects and corrosion sites, BTA can be rapidly released to form a protective complex film on the metal surface, so as to inhibit the further propagation of corrosion.

3.3. Effects of BTA-SiO₂@Al₂O₃ incorporation on the morphology and properties of composite coatings

To systematically elucidate the regulatory effect of BTA-SiO₂@Al₂O₃ composite fillers on the microstructure of waterborne epoxy coatings, the neat WEP coating was first employed as the blank control to characterize its intrinsic surface and cross-sectional morphologies as well as inherent structural defects. Subsequently, BTA-SiO₂@Al₂O₃-WEP-20 was selected as the representative sample to conduct a comparative investigation on the morphological evolution of composite coatings before and after filler incorporation.

As shown in Fig. 4a, the pure WEP coating exhibits a smooth, continuous surface without obvious particle protrusions or macroscopic defects, confirming that the aqueous epoxy resin can form a relatively intact film structure after curing. However, the pure WEP coating suffers from inherent structural limitations: during the curing process, the evaporation of water and volatile organic compounds inevitably leaves

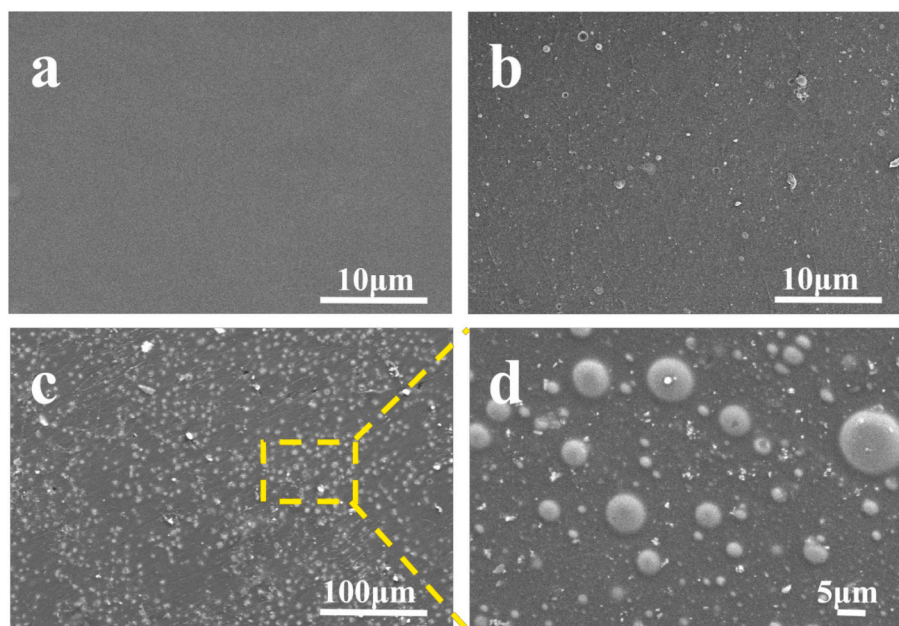


Fig. 4. FESEM images of (a) the surface morphology of neat WEP coating, (b) the surface morphology of BTA-SiO₂@Al₂O₃-WEP-20 composite coating, (c) the cross-sectional morphology of BTA-SiO₂@Al₂O₃-WEP-20 composite coating, and (d) the high-magnification cross-sectional morphology of the yellow dashed region in (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

interconnected micropores (diameter: 50–200 nm) and free volume defects in the resin matrix. These defects act as preferential permeation pathways for corrosive media (H₂O, O₂, and Cl[−]), allowing them to gradually penetrate to the metal substrate even in the absence of macroscopic cracks. Additionally, the pure WEP coating shows a typical brittle fracture characteristic with a flat cross-section, indicating poor resistance to crack propagation under mechanical stress or thermal cycling. After incorporating BTA-SiO₂@Al₂O₃ composite microspheres, the coating surface presents uniformly distributed micro-nano protrusions (Fig. 4b), which correspond to the submicron-sized composite microspheres embedded in the resin matrix. No obvious agglomeration of microspheres is observed, demonstrating that the surface modification with SiO₂ and BTA significantly improves the dispersibility of Al₂O₃ in the aqueous epoxy system. This improvement is attributed to two synergistic effects: Firstly, the amorphous SiO₂ shell introduces abundant silanol groups (Si–OH) on the microsphere surface, which form strong hydrogen bonds with the epoxy groups and hydroxyl groups in the WEP matrix; Secondly, the absorbed BTA molecules contain aromatic rings and amino groups, which enhance the interfacial compatibility between the inorganic filler and the organic resin via π – π stacking and van der Waals interactions. Most microspheres are completely wrapped by the epoxy resin, forming a tight filler-resin interface without obvious gaps, which effectively avoids the formation of interfacial defects that would accelerate corrosion medium penetration.

The cross-sectional FESEM image (Fig. 4c) further reveals that the BTA-SiO₂@Al₂O₃ microspheres are uniformly dispersed throughout the entire coating thickness, and the coating maintains a continuous, dense structure without penetrating cracks or large voids. Compared with the pure WEP coating, the cross-section of the composite coating shows a rougher fracture surface with obvious crack deflection and branching, indicating that the composite microspheres effectively absorb fracture energy and improve the toughness of the coating. The high-magnification cross-sectional image (Fig. 4d) clearly shows that the composite microspheres are tightly embedded in the resin matrix, forming a three-dimensional interpenetrating barrier structure. This structure exerts a significant “labyrinth effect”: the randomly distributed spherical microspheres force corrosive media to take tortuous diffusion paths instead of straight-line penetration.

This densification effect not only blocks the direct permeation channels of corrosive media but also improves the mechanical integrity of the coating. It is worth noting that no obvious interfacial debonding is observed between the microspheres and the resin matrix, which confirms the excellent interfacial adhesion achieved by the core-shell modification strategy. This strong interfacial bonding is crucial for maintaining the long-term stability of the barrier structure, as it prevents the formation of interfacial gaps that would act as fast diffusion pathways for corrosive ions during prolonged immersion.

3.4. Thermal property enhancement of waterborne epoxy coatings via BTA-SiO₂@Al₂O₃ core-shell microspheres

3.4.1. TGA measurement

TGA measurement was employed to systematically evaluate the thermal degradation behavior and thermal stability of the neat waterborne epoxy (WEP) coating, 25 wt% pristine α -Al₂O₃ filled WEP coating (Al₂O₃-WEP-25), and 25 wt% BTA-SiO₂@Al₂O₃ composite filler filled WEP coating (BTA-SiO₂@Al₂O₃-WEP-25), and the results are shown in Fig. 5. The 5% mass loss temperatures (initial decomposition temperatures) of each coating are indicated by the dashed lines, which is a core indicator for evaluating the thermal stability of polymer materials and represents the critical temperature at which significant thermal degradation of the material begins [33].

All coatings exhibited slight mass loss (<5%) in the temperature range of 25–200 °C, which was mainly attributed to the removal of a small amount of residual solvent and physically adsorbed water after coating curing. After entering the main thermal degradation stage, the thermal stabilities of the three coatings showed significant differences: the 5% mass loss temperature of the neat WEP coating was only 193.25 °C, indicating its poorest thermal stability; after the introduction of pristine α -Al₂O₃ microspheres, the initial decomposition temperature of Al₂O₃-WEP-25 increased to 208.22 °C. This was because the high-melting-point and low-thermal-conductivity α -Al₂O₃ microspheres formed a physical barrier in the resin matrix, inhibiting the rapid conduction of heat and the diffusion of small-molecule degradation products. In contrast, the initial decomposition temperature of the BTA-SiO₂@Al₂O₃-WEP-25 coating was significantly increased to

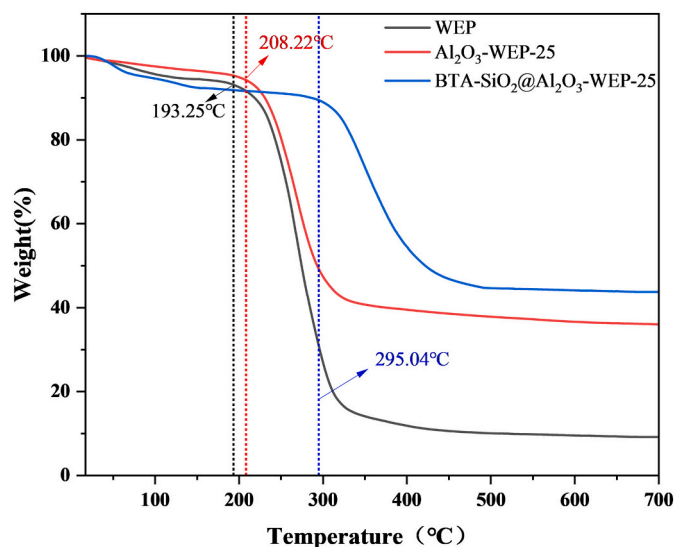


Fig. 5. Thermogravimetric analysis (TGA) curves of neat waterborne epoxy (WEP) coating, 25 wt% pristine α - Al_2O_3 filled WEP coating (Al_2O_3 -WEP-25), and 25 wt% BTA- SiO_2 @ Al_2O_3 composite filler filled WEP coating (BTA- SiO_2 @ Al_2O_3 -WEP-25). The 5% mass loss temperatures (initial decomposition temperatures) of each coating are indicated by the dashed lines.

295.04 °C, which was 101.79 °C higher than that of the neat WEP coating and 86.82 °C higher than that of the Al_2O_3 -WEP-25 coating, demonstrating excellent thermal stability. This remarkable improvement originated from the synergistic effect of the BTA- SiO_2 @ Al_2O_3 core-shell structure: the continuous amorphous SiO_2 shell formed micro thermal barrier units, further attenuating heat transfer; meanwhile, the abundant silanol groups (Si-OH) on the surface of the SiO_2 shell formed a high-density hydrogen-bonding crosslinking network with the hydroxyl and amino groups in the epoxy resin matrix, restricting the thermal motion of epoxy molecular chains and delaying the cleavage of the polymer backbone.

In the later stage of high-temperature thermal degradation, all three coatings entered a mass-stable plateau stage: the neat WEP coating basically maintained a constant mass after approximately 400 °C, with a final residual rate of about 10%, which was mainly the carbonized product formed by the thermal degradation of the epoxy resin; the Al_2O_3 -WEP-25 coating tended to be stable after approximately 450 °C, with a final residual rate of about 36%, and the residual substances included α - Al_2O_3 inorganic fillers and carbonized matrix; the BTA- SiO_2 @ Al_2O_3 coating entered a stable plateau after approximately 500 °C, with a final residual rate as high as about 44%. This was because its core-shell structure not only retained the two inorganic fillers of α - Al_2O_3 and SiO_2 but also promoted the carbonization of the epoxy resin through interfacial interactions, forming a denser carbon layer and further improving the structural stability at high temperatures.

3.4.2. DSC measurement

To further investigate the regulatory mechanism of BTA- SiO_2 @ Al_2O_3 core-shell composite fillers on the thermal motion behavior of molecular chains in waterborne epoxy coatings (WEP), DSC was employed to determine the glass transition temperature (T_g) of composite coatings with various filler loadings. As shown in Fig. 6, the neat WEP coating cured with waterborne polyamide exhibited a T_g of 29.59 °C. With the gradual increase in the loading of BTA- SiO_2 @ Al_2O_3 from 5 wt% to 25 wt %, the glass transition temperature (T_g) of the cured composite coatings first rises and then decreases, peaking at 37.9 °C when the filler loading is 20 wt%.

The mechanism underlying the T_g enhancement can be attributed to the strong interfacial interaction between the fillers and the resin matrix

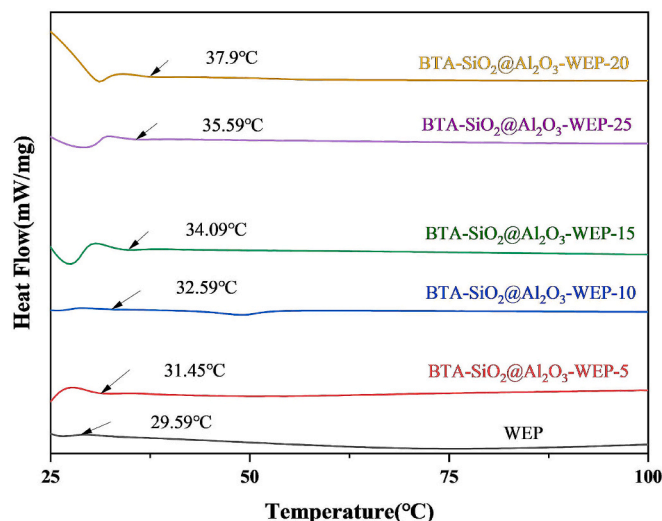


Fig. 6. DSC curves of neat waterborne epoxy (WEP) coating and BTA- SiO_2 @ Al_2O_3 -WEP composite coatings with filler loadings of 5, 10, 15, 20, and 25 wt%. The glass transition temperatures (T_g) of each coating are indicated by the arrows.

[34]. FESEM characterization confirmed that the surface of Al_2O_3 microspheres was successfully coated with a dense amorphous SiO_2 shell, which was rich in abundant active silanol (Si-OH) groups. These functional groups could form a high-density hydrogen-bonding crosslinking network with hydroxyl, amino, and ether groups in the WEP matrix, significantly restricting the thermal mobility of epoxy molecular chains and thus increasing the T_g of the composite coatings. The elevated T_g not only contributed to the improved hardness and mechanical stability of the coatings but also further inhibited the diffusion and penetration of corrosive media in the three-dimensional polymer network, thereby synergistically enhancing the long-term anticorrosion performance of the coatings.

3.5. Mechanical property enhancement of waterborne epoxy coatings via BTA- SiO_2 @ Al_2O_3 core-shell microspheres

Combined with the above DSC and TGA thermal analysis results, BTA- SiO_2 @ Al_2O_3 fillers can construct interfacial hydrogen-bonding networks, restrict the mobility of epoxy molecular chains, and improve the compactness and structural rigidity of coatings. The internal molecular chain behavior and interfacial microstructure fundamentally govern the macroscopic mechanical properties. Accordingly, the mechanical performances of composite coatings were systematically evaluated in terms of hardness, flexibility, impact resistance, adhesion and abrasion resistance. All tests were performed in triplicate, and the average values with standard deviations are summarized in Table 1.

Pencil hardness increases progressively with filler loading, advancing from B for the neat WEP to 3H at loadings of 20 and 25 wt%. This stiffening effect is accompanied by a gradual decline in flexibility and adhesion strength as more inorganic filler is introduced. Flexibility remains at 0.5 mm for loadings ≤ 10 wt%, increases to 1.0 mm at 15–20 wt%, and drops further to 1.5 mm at 25 wt%. Adhesion strength decreases moderately with rising filler content but stays above 2.0 MPa for all formulations. Impact resistance remains unchanged across all samples, with all coatings passing the 50 kg·cm test without cracking or delamination, indicating that filler incorporation does not compromise impact tolerance within the tested range.

As for abrasion resistance, a critical service property for protective coatings, the cumulative mass loss after 450 abrasion cycles shows a typical volcano-type trend with filler loading. The neat WEP coating exhibits the poorest wear resistance with the highest mass loss, while

Table 1
Mechanical properties of the composite coatings with various BTA-SiO₂@Al₂O₃ content.

Mechanical properties	WEP	BTA-SiO ₂ @Al ₂ O ₃ -WEP-5	BTA-SiO ₂ @Al ₂ O ₃ -WEP-10	BTA-SiO ₂ @Al ₂ O ₃ -WEP-15	BTA-SiO ₂ @Al ₂ O ₃ -WEP-20	BTA-SiO ₂ @Al ₂ O ₃ -WEP-25
Mechanical properties Samples						
Pencil hardness	B	H	H	2H	3H	3H
Flexibility(mm)	0.5	0.5	0.5	1	1	1.5
Impact resistance(kg. cm)	50	50	50	50	50	50
Adhesion strength (Mpa)	2.95	2.75	2.46	2.21	2.14	2.09
Abrasion mass loss / g	0.102 ± 0.008	0.076 ± 0.005	0.048 ± 0.004	0.030 ± 0.003	0.021 ± 0.002	0.026 ± 0.003

incorporation of BTA-SiO₂@Al₂O₃ fillers markedly reduces material loss. At 20 wt% loading, the abrasion mass loss reaches a minimum of 0.021 g, corresponding to a 79.4% reduction compared with the neat WEP. This improvement is attributed to the rigid Al₂O₃ framework carrying contact loads and the hydrogen-bonded interfacial network restricting polymer chain sliding under friction. When loading is increased to 25 wt%, however, abrasion mass loss rebounds to 0.026 g, indicating that excess filler impairs wear performance. The full abrasion mass loss curves with increasing cycles are provided in Fig. S1 in the supporting information.

Incorporating inorganic fillers into waterborne epoxy entails a clear trade-off between thermal-mechanical reinforcement and property deterioration at high loadings. Thermal properties improve monotonically with filler content, reaching maximum enhancement at 25 wt %-a 101.79 °C rise in initial decomposition temperature and an 8.31 °C increase in T_g -because the inherent thermal stability of the inorganic phase and interfacial hydrogen bonding persist even at high filler fractions. In contrast, comprehensive mechanical performance follows a volcano-shaped trend. From 0 to 20 wt% loading, the performance gains are substantial: hardness rises by four grades and abrasion mass loss drops by 79.4%, while flexibility (1.0 mm) and adhesion (2.14 MPa) remain within acceptable service ranges. Increasing the loading from 20 to 25 wt% yields no further improvement in hardness, yet causes a 50% drop in flexibility (from 1.0 to 1.5 mm), a 2.3% reduction in adhesion, and a 23.8% rebound in abrasion mass loss. The marginal gain in thermal stability from this additional 5 wt% filler is clearly outweighed by the deterioration in key mechanical properties.

This performance deterioration above 20 wt% arises from interrelated microstructural effects. At high filler fractions, the reduced interparticle distance and strong van der Waals attractions between alumina microspheres promote the formation of large agglomerates that act as internal stress concentration sites, initiating crack propagation under bending or mechanical deformation and thereby reducing coating flexibility. The epoxy matrix cannot fully wet and encapsulate overcrowded filler particles, leaving interfacial voids and partial debonding at the agglomerate-matrix boundaries; these defects weaken the overall bonding between the coating film and the steel substrate, lowering adhesion strength and promoting material spalling during abrasion. Additionally, a high volume fraction of inorganic particles interrupts the continuity of the three-dimensional epoxy-curing agent crosslinking network, reducing the intrinsic toughness of the polymer matrix and further compromising deformation resistance.

On balance, the 20 wt% loading achieves the optimal balance of thermal stability, mechanical performance, and anticorrosion protection (detailed in Section 3.6). At this loading, the coating retains near-maximal thermal stability, exhibits the highest hardness and abrasion resistance, and maintains adequate flexibility and interfacial adhesion, enabling simultaneous enhancement of multiple critical service properties for waterborne epoxy coatings.

3.6. Anticorrosion performance enhancement of waterborne epoxy coatings via BTA-SiO₂@Al₂O₃ core-shell microspheres

Electrochemical impedance spectroscopy (EIS) is a core electrochemical technique for characterizing the protective performance of organic coatings, elucidating the permeation process of corrosive media, and revealing the failure mechanism of coating systems. To systematically investigate the regulatory effect of BTA-SiO₂@Al₂O₃ core-shell microspheres incorporation on the anticorrosion performance of waterborne epoxy (WEP) composite coatings, the content of WEP matrix was fixed, and the loading of BTA-SiO₂@Al₂O₃ core-shell microspheres was gradually varied in the range of 5–25 wt% in this work. Six groups of coated specimens were prepared, where sample Fig. 7 a was the neat WEP coating, and samples Fig. 7 b–f corresponded to the composite coatings with filler loadings of 5, 10, 15, 20, and 25 wt%, respectively. All specimens were immersed in 3.5 wt% NaCl aqueous solution (simulated seawater), and EIS spectra were collected at predefined immersion time points of 1, 24, 48, 96, and 240 h. The initial physical barrier performance, long-term protective stability, and interfacial corrosion evolution mechanism of the composite coatings were systematically analyzed based on the acquired EIS data.

3.6.1. Nyquist plot analysis: evolution of coating barrier integrity

The radius of the capacitive arc in the Nyquist plot directly reflects the polarization resistance of the coating system, where a larger radius indicates a higher charge transfer resistance and superior corrosion resistance. [31] All coatings exhibited capacitive arc radii greater than 10⁶ Ω·cm² at the initial immersion stage (1 h), indicating that the as-cured coatings possessed a dense structure without obvious macroscopic defects. Among them, the neat waterborne epoxy (WEP) coating (sample a) showed the smallest capacitive arc radius, while the introduction of BTA-SiO₂@Al₂O₃ composite fillers significantly increased the arc radius. This phenomenon can be attributed to the “labyrinth effect” of the composite fillers, which effectively prolonged the diffusion paths of corrosive media such as H₂O, O₂, and Cl⁻ within the coating. However, the performance evolution patterns of coatings with different filler loadings during long-term immersion were significantly different.

For samples b, c, and d (corresponding to 5, 10, and 15 wt% filler loadings, respectively) with low BTA-SiO₂@Al₂O₃ content, their initial barrier properties were significantly improved compared with the neat WEP coating, but their long-term protective stability was generally poor. After 48 h of immersion, a distinct second time constant appeared in the high-frequency region of the Nyquist plots for these three groups of samples, indicating that corrosive media had penetrated to the coating-metal interface through tiny inherent defects inside the coating and initiated initial corrosion of the substrate. By 240 h of immersion, the capacitive arc diameters of samples b, c, and d all decreased significantly, and the protective performance of the coatings showed varying degrees of attenuation. This is because at low filler loadings, the

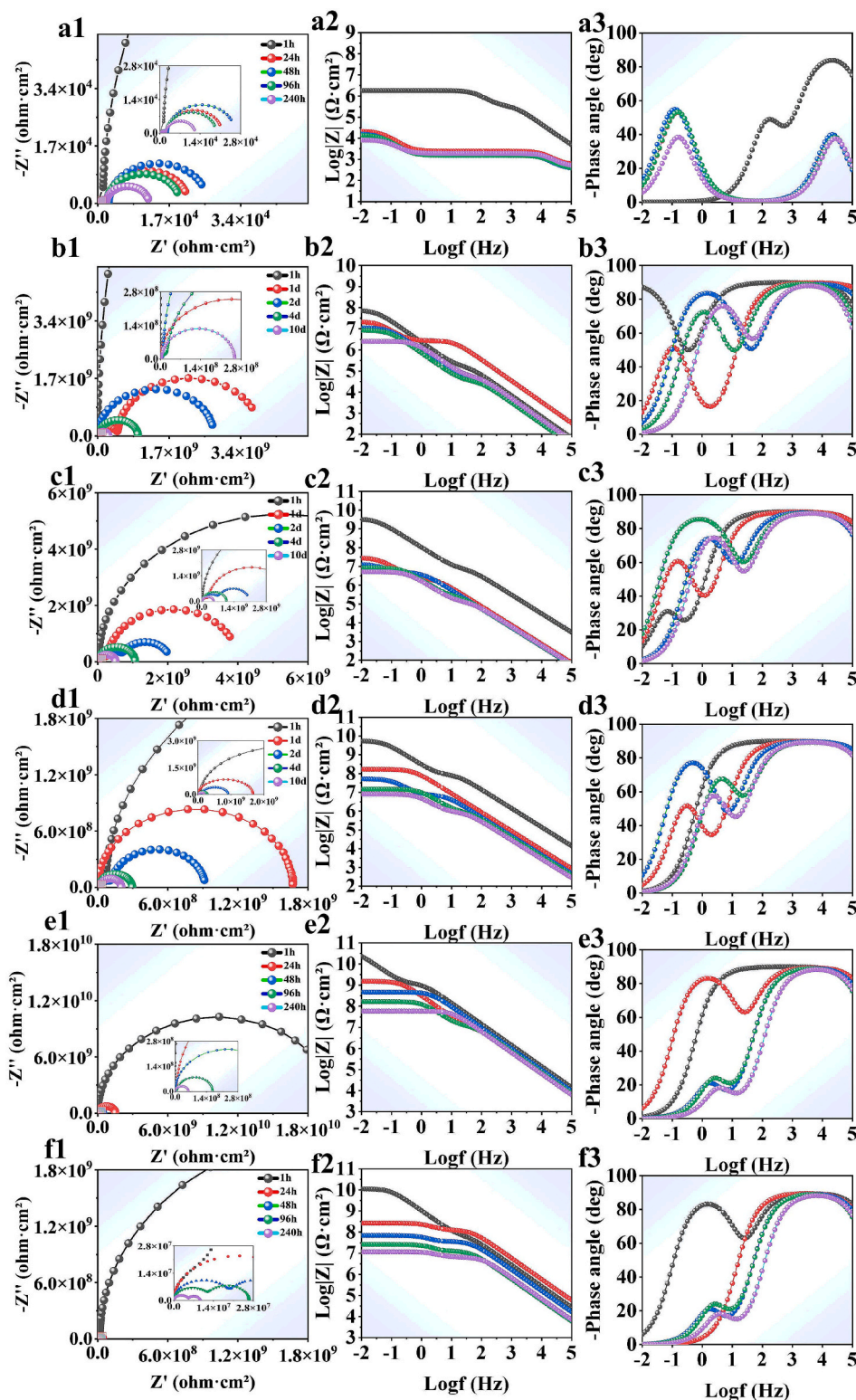


Fig. 7. Electrochemical impedance spectroscopy (EIS) spectra of (a) neat WEP coating, (b) BTA-SiO₂@Al₂O₃-WEP-5, (c) BTA-SiO₂@Al₂O₃-WEP-10, (d) BTA-SiO₂@Al₂O₃-WEP-15, (e) BTA-SiO₂@Al₂O₃-WEP-20, and (f) BTA-SiO₂@Al₂O₃-WEP-25 composite coatings immersed in 3.5 wt% NaCl solution for 1 h, 24 h, 48 h, 96 h, and 240 h. For each sample: (1) Nyquist plots (the insets show the enlarged views of the Nyquist plots in the low-impedance region), (2) Bode magnitude plots, and (3) Bode phase angle plots.

composite fillers cannot form a continuous three-dimensional barrier network, and corrosive media can still slowly penetrate through the resin matrix regions between the fillers. Moreover, the limited release amount of BTA corrosion inhibitor is insufficient to completely inhibit

the interfacial corrosion reactions.

Sample f (25 wt% filler loading) had a higher initial capacitive arc diameter than the neat WEP coating, but its performance degradation rate was the fastest among all samples. After 24 h of immersion, its

capacitive arc diameter plummeted to $10^7 \Omega\text{-cm}^2$; after 48 h, it already exhibited obvious double capacitive arc characteristics, indicating that the substrate corrosion was relatively severe; by 240 h, the capacitive arc diameter was only $10^7 \Omega\text{-cm}^2$, and the protective performance of the coating was largely compromised. The fundamental reason is that excessive filler loading leads to severe agglomeration between particles, generating a large number of interfacial pores and microcracks inside the coating. These defects act as rapid penetration channels for corrosive media, accelerating the failure process of the coating.

3.6.2. Bode magnitude plot analysis: quantitative evaluation of long-term protective performance

The low-frequency impedance modulus at 0.01 Hz ($|Z|_{0.01\text{Hz}}$) in the Bode magnitude plot is a core quantitative indicator for evaluating the overall protective performance of organic coatings [31]. Its value comprehensively reflects the physical barrier capability of the coating matrix and the electrochemical corrosion inhibition effect at the coating-metal interface, and is positively correlated with the long-term corrosion resistance of the coating. Consistent with the results of Nyquist plot analysis, the $|Z|_{0.01\text{Hz}}$ of the neat waterborne epoxy (WEP) coating was only $1.2 \times 10^6 \Omega\text{-cm}^2$ after 1 h of initial immersion, indicating that its initial physical barrier capability was insufficient due to inherent microporous defects caused by the volatilization of water and small molecules during the curing process. After the introduction of BTA-SiO₂@Al₂O₃ composite fillers, the initial low-frequency impedance of the coatings exhibited a significant “first increase then decrease” trend. When the filler loading was gradually increased from 5 wt% to 20 wt%, the $|Z|_{0.01\text{Hz}}$ was significantly enhanced from $3.5 \times 10^7 \Omega\text{-cm}^2$ to $9.2 \times 10^9 \Omega\text{-cm}^2$ (nearly 3 orders of magnitude higher than that of the neat WEP coating), while it decreased to $2.1 \times 10^8 \Omega\text{-cm}^2$ when the filler loading was further increased to 25 wt%, confirming that there exists a clear optimal loading threshold for the enhancement effect of composite fillers on the corrosion resistance of coatings. During the 240 h continuous immersion process, the evolution patterns of $|Z|_{0.01\text{Hz}}$ for coatings with different filler loadings showed significant differences: the low-frequency impedance of the neat WEP coating decreased continuously and sharply, dropping below $10^4 \Omega\text{-cm}^2$ at 240 h, and the coating basically lost its protective function; although the low-loading (5–15 wt %) filler-modified coatings showed improved initial impedance, their long-term stability was insufficient due to the failure to form a continuous three-dimensional barrier network and the limited release amount of corrosion inhibitor, and their $|Z|_{0.01\text{Hz}}$ decreased to $10^5/10^6 \Omega\text{-cm}^2$ at 240 h; the high-loading (25 wt%) sample suffered from the most severe performance degradation, with its $|Z|_{0.01\text{Hz}}$ being only $8.5 \times 10^5 \Omega\text{-cm}^2$ at 240 h, which was attributed to the severe agglomeration effect caused by excessive fillers, generating a large number of interfacial pores and microcracks that acted as rapid penetration channels for corrosive media. In sharp contrast, the sample with the optimal loading of 20 wt% exhibited excellent long-term protective stability, and its $|Z|_{0.01\text{Hz}}$ still remained at $6.3 \times 10^7 \Omega\text{-cm}^2$ at 240 h (more than 2 orders of magnitude higher than that of the neat WEP coating). Its superior performance originated from the synergistic protective mechanism of “physical barrier-chemical corrosion inhibition”: the uniformly dispersed composite fillers constructed a continuous and dense three-dimensional barrier network, which significantly prolonged the diffusion paths of corrosive media through the “labyrinth effect”; meanwhile, BTA molecules adsorbed on the surface of the SiO₂ shell were slowly released to the coating-metal interface with the penetration of corrosive media, and chelated with Fe²⁺/Fe³⁺ ions dissolved from the substrate to form a dense passivation film, effectively inhibiting the occurrence and development of interfacial electrochemical reactions.

3.6.3. Bode phase angle plot analysis: coating capacitive behavior and interfacial corrosion evolution

The magnitude, number, and frequency position of phase angle peaks in the Bode phase angle plot intuitively reflect the time constant

characteristics of the coating-metal system [35,36]. A phase angle peak closer to -90° with a wider frequency coverage indicates more significant pure capacitive behavior of the system, a denser coating structure with fewer defects, and superior physical barrier performance. The appearance of a second time constant signifies that corrosive media have penetrated to the coating-metal interface and initiated electrochemical corrosion reactions of the substrate. Highly consistent with the analysis results of Nyquist plots and Bode magnitude plots, the phase angle evolution patterns of coatings with different filler loadings showed significant differences, clearly revealing the dynamic changes of the internal coating structure and interfacial state. The neat WEP coating exhibited insufficient initial compactness due to residual micropores from curing, showing a relatively low phase angle peak with a narrow frequency range at the initial immersion stage. A double time constant formed rapidly after 24 h of immersion, indicating that corrosive media had quickly penetrated to the interface through inherent defects, and interfacial corrosion reactions became the core factor dominating the failure of coating protection. Samples b, c, and d (5–15 wt%) with low BTA-SiO₂@Al₂O₃ loading initially showed a single high phase angle peak, indicating a relatively dense initial coating structure. However, with prolonged immersion time, the phase angle peak gradually decreased and the frequency range narrowed, and a second time constant appeared successively within 48–96 h. The interfacial corrosion process developed gradually from slow to fast, and the attenuation rate of protective performance slightly accelerated with increasing filler loading. This is because low-content fillers cannot form a continuous barrier network, corrosive media can still slowly penetrate through the resin matrix regions, and the increased interfacial defects caused by higher filler loading further accelerate medium penetration. The high-loading sample f (25 wt%) exhibited double time constant characteristics even at the initial immersion stage, and the phase angle peak shifted rapidly to the high-frequency direction, indicating that interfacial pores and microcracks generated by excessive filler agglomeration had become initial defects, leading to rapid penetration of corrosive media to the interface at the early stage of immersion and rapid failure of the coating structure. In sharp contrast, the optimal-loading sample e (20 wt %) always maintained a single high phase angle peak throughout the 240 h immersion period, with the phase angle peak stably remaining above -80° and covering a wide frequency range, and no obvious evolution of double time constants was observed. This indicates that the capacitive behavior of the coating was stable, corrosive media did not penetrate to the coating-metal interface, and interfacial electrochemical reactions were effectively inhibited, fully demonstrating the synergistic protective effect of the continuous three-dimensional physical barrier network constructed by uniformly dispersed composite fillers and the controlled release of BTA corrosion inhibitor.

3.6.4. Equivalent circuit fitting and interfacial corrosion kinetics analysis

Although the qualitative analysis of Nyquist plots and Bode plots can intuitively reveal the evolution trend and overall law of coating protective performance, it cannot quantitatively distinguish the independent contributions of coating bulk physical barrier and interfacial electrochemical corrosion, nor can it accurately quantify the variation amplitude of key kinetic parameters during the corrosion process [37,38]. To deeply analyze the microscopic mechanism of coating failure and quantitatively evaluate the regulatory effect of composite fillers on the physical barrier capability of coatings and the interfacial corrosion inhibition effect, the electrochemical impedance spectra of the neat waterborne epoxy (WEP) coating and the optimal 20 wt% BTA-SiO₂@Al₂O₃ composite coating immersed in 3.5 wt% NaCl solution for different durations were quantitatively fitted using the two-time-constant equivalent circuit model $R_s(CPE_c(R_c(CPE_d(R_{ct}))))$ shown in Fig. 8(a).

A unified dual-time-constant equivalent circuit model was adopted for all EIS spectra to ensure consistent fitting criteria and reliable quantitative comparison across samples with different filler loadings

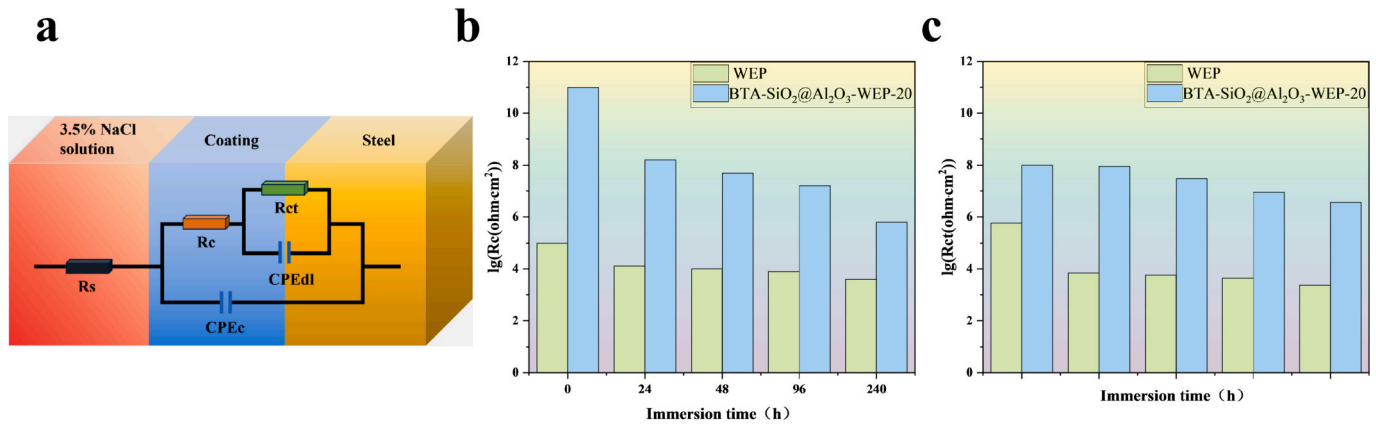


Fig. 8. (a) Equivalent circuit model used for EIS data fitting; evolution of (b) $\lg(R_c)$ and (c) $\lg(R_{ct})$ for neat WEP and BTA-SiO₂@Al₂O₃-WEP-20 composite coatings during immersion in 3.5 wt% NaCl solution. Detailed fitted parameters are listed in Table 2. (*In this equivalent circuit: R_s represents the solution resistance of 3.5 wt % NaCl electrolyte; CPE_c is the constant phase element used to describe the non-ideal capacitive behavior of the coating bulk, defined by the admittance constant $Y_{0,c}$ (unit: $\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-n_c}$) and the dimensionless dispersion exponent n_c ; R_c reflects the total resistance of conductive channels formed by the penetration of corrosive media into the coating, directly characterizing the physical barrier capability of the coating; CPE_{dl} is the constant phase element corresponding to the electric double-layer capacitance at the coating-metal interface, with parameters $Y_{0,d}$ and n_d ; R_{ct} represents the charge transfer resistance of interfacial electrochemical reactions, whose value is strictly inversely proportional to the corrosion rate of the metal substrate and serves as a core parameter for evaluating interfacial electrochemical corrosion kinetics.)

and immersion durations. For coatings that maintain a single capacitive arc feature after long-term immersion, this apparent spectral characteristic originates from the highly suppressed interfacial corrosion process: the charge transfer resistance at the metal/coating interface remains at an extremely high level, such that the interfacial electrochemical response is masked by the dominant coating bulk barrier response and cannot be fully resolved within the tested frequency range. Under this condition, the dual-time-constant model is mathematically compatible with single-time-constant systems-the fitting parameters automatically converge to a state where the interfacial time constant contributes negligibly to the total impedance, without introducing additional systematic errors.

The evolution of $\lg(R_c)$ and $\lg(R_{ct})$ with immersion time is visualized in Fig. 8(b) and (c), respectively. All fitted electrochemical parameters and the corresponding chi-squared (χ^2) fitting errors are summarized in Table 2. All χ^2 values are in the range of 1.2×10^{-4} – 8.5×10^{-4} , indicating high reliability and good goodness of fit between the equivalent circuit model and experimental data.

The fitting results showed that the initial R_c and R_{ct} of the neat WEP coating were only $1.04 \times 10^5 \Omega \cdot \text{cm}^2$ and $7.89 \times 10^5 \Omega \cdot \text{cm}^2$, respectively, and exhibited a continuous and sharp downward trend with increasing immersion time, dropping to $5.94 \times 10^3 \Omega \cdot \text{cm}^2$ and $3.47 \times 10^3 \Omega \cdot \text{cm}^2$ after 240 h of immersion, with a decrease of more than 2 orders of magnitude. This result confirms that the neat waterborne epoxy coating contains a large number of inherent microporous defects after curing due to the volatilization of water and small molecules. Corrosive media can rapidly penetrate to the coating-metal interface through these

defects at the early stage of immersion, triggering and continuously intensifying interfacial electrochemical reactions, which ultimately leads to the rapid attenuation of the coating's protective performance.

In sharp contrast, the initial R_c and R_{ct} of the 20 wt% BTA-SiO₂@Al₂O₃ composite coating were as high as $1.02 \times 10^{11} \Omega \cdot \text{cm}^2$ and $1.01 \times 10^8 \Omega \cdot \text{cm}^2$, respectively, representing an increase of nearly 6 and 3 orders of magnitude compared with the neat WEP coating. This intuitively verifies that the introduction of composite fillers significantly enhances the initial physical barrier capability and interfacial protective effect of the coating. Although a small amount of interfacial defects caused a slightly faster decline rate of R_c and R_{ct} than the ideal state, their values still remained at $8.09 \times 10^5 \Omega \cdot \text{cm}^2$ and $6.43 \times 10^6 \Omega \cdot \text{cm}^2$ after 240 h of immersion, which were much higher than those of the neat WEP coating at the same time point. This indicates that even with minor structural inhomogeneity, the uniformly dispersed BTA-SiO₂@Al₂O₃ composite fillers can still significantly prolong the diffusion paths of corrosive media within the coating through the “labyrinth effect”. Meanwhile, BTA corrosion inhibitors adsorbed on the surface of the SiO₂ shell can be slowly released to the interface with the penetration of corrosive media, chelating with Fe ions dissolved from the substrate to form a dense passivation film, effectively inhibiting the progress of interfacial electrochemical reactions and thus greatly improving the long-term protective stability of the coating.

3.6.5. Potentiodynamic polarization curve analysis

Potentiodynamic (Tafel) polarization curves are the core method for quantitatively evaluating the kinetic behavior of metal corrosion. They

Table 2

Fitted EIS parameters of neat WEP and BTA-SiO₂@Al₂O₃-WEP-20 coatings after different immersion times in 3.5 wt% NaCl solution.

Sample	t/h	$R_s/\Omega \cdot \text{cm}^2$	$Q_c \cdot Y_0/\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^{-n}$	$Q_c \cdot n$	$R_c/\Omega \cdot \text{cm}^2$	$Q_{dl} \cdot Y_0/\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^{-n}$	$Q_{dl} \cdot n$	$R_{ct}/\Omega \cdot \text{cm}^2$
Neat WEP	1	7.68	4.11×10^{-9}	7.81×10^{-1}	1.04×10^5	2.34×10^{-4}	8.20×10^{-1}	7.89×10^5
	24	1.03	5.61×10^{-7}	5.85×10^{-1}	1.37×10^4	1.70×10^{-4}	7.62×10^{-1}	8.06×10^3
	48	6.98	6.55×10^{-7}	5.74×10^{-1}	1.01×10^4	1.73×10^{-4}	7.72×10^{-1}	7.74×10^3
	96	7.09	5.62×10^{-7}	5.89×10^{-1}	9.16×10^3	1.86×10^{-4}	7.95×10^{-1}	6.43×10^3
	240	9.98	5.61×10^{-7}	5.94×10^{-1}	5.94×10^3	3.53×10^{-4}	7.78×10^{-1}	3.47×10^3
BTA-SiO ₂ @Al ₂ O ₃ -WEP-20	1	1.49	3.14×10^{-10}	9.46×10^{-1}	1.02×10^{11}	3.68×10^{-10}	9.23×10^{-1}	1.01×10^8
	24	6.42	3.00×10^{-10}	9.45×10^{-1}	3.13×10^8	6.61×10^{-10}	7.29×10^{-1}	1.89×10^8
	48	1.37	1.67×10^{-10}	1.00×10^0	7.72×10^7	4.98×10^{-8}	8.62×10^{-1}	5.09×10^7
	96	2.70	4.04×10^{-10}	9.40×10^{-1}	1.98×10^7	3.02×10^{-9}	5.26×10^{-1}	1.08×10^7
	240	2.09	7.15×10^{-10}	8.93×10^{-1}	8.09×10^5	2.27×10^{-5}	8.70×10^{-1}	8.43×10^6

can directly obtain key electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (i_{corr}), and accurately calculate the metal corrosion rate through Faraday's law, providing a direct quantitative basis for evaluating the protective performance of coatings [39]. To further verify the results of electrochemical impedance spectroscopy and salt spray tests, the potentiodynamic polarization behavior of the neat WEP coating and composite coatings with different BTA-SiO₂@Al₂O₃ contents after immersion in 3.5 wt% NaCl solution for 240 h was tested. The results are shown in Fig. 9, and the fitted electrochemical parameters and corrosion rates are presented in the corresponding table (Table S1).

The fitting results showed that with the gradual increase of BTA-SiO₂@Al₂O₃ composite filler content from 5 wt% to 25 wt%, the corrosion potential of the composite coatings first shifted positively and then drifted negatively (indicating the corrosion tendency was weakened at first and then enhanced), and the corrosion current density decreased firstly and then increased, and the corrosion rate significantly dropped from 1.467×10^{-4} mm/year to 9.786×10^{-6} mm/year. Compared with the neat WEP coating (corrosion rate 2.257×10^{-4} mm/year), all composite coatings exhibited remarkably improved corrosion resistance. Among them, when the filler content was 20 wt%, the composite coating achieved the minimum corrosion current density and the lowest corrosion rate, demonstrating the optimal corrosion resistance.

This enhancement effect of corrosion resistance can be attributed to a dual synergistic mechanism: (1) The uniformly dispersed BTA-SiO₂@Al₂O₃ composite fillers possess excellent physical barrier properties, forming a continuous three-dimensional barrier network in the resin matrix, which significantly prolongs the diffusion path of corrosive media through the "labyrinth effect" and simultaneously inhibits the progress of cathodic and anodic electrochemical reactions; (2) The BTA corrosion inhibitor adsorbed on the surface of the composite microspheres can be slowly released with the penetration of corrosive media, and chelate with Fe²⁺/Fe³⁺ ions dissolved from the substrate to form a dense passivation film, effectively preventing the further development of corrosion.

3.6.6. Salt spray accelerated corrosion test

To further verify the reliability of the electrochemical test results and evaluate the practical protective performance of the coatings in a simulated marine atmospheric environment, a 240 h neutral salt spray

accelerated corrosion test was conducted on the neat WEP coating and BTA-SiO₂@Al₂O₃-WEP composite coatings with different filler loadings (test conditions: 5 wt% NaCl solution, pH = 6.5–7.2, chamber temperature 35 ± 2 °C, sedimentation rate 1–2 mL/(80 cm²·h)). The surface corrosion morphologies of different coatings after salt spray exposure are shown in Fig. S2.

After 240 h of salt spray exposure, the coatings exhibited significantly different degrees of corrosion damage. A large amount of yellowish-brown rust appeared in the scratch area of the neat waterborne epoxy (WEP) coating, and the corrosion products diffused extensively to both sides of the scratch, accompanied by obvious peeling between the coating and the substrate, indicating that the protective performance of the neat WEP coating had completely failed. With the increase of BTA-SiO₂@Al₂O₃ composite filler loading from 5 wt% to 20 wt%, the salt spray resistance of the coatings gradually improved: obvious accumulation of corrosion products was observed at the scratches of BTA-SiO₂@Al₂O₃-WEP-5 and BTA-SiO₂@Al₂O₃-WEP-10 coatings, and the corrosion tended to diffuse to the surrounding matrix; the corrosion degree at the scratch of BTA-SiO₂@Al₂O₃-15 coating was alleviated, but a small amount of rust was still visible. In contrast, the scratch area of the optimal BTA-SiO₂@Al₂O₃-WEP-20 coating only presented a negligible amount of corrosion products after 240 h of salt spray exposure, with no obvious corrosion propagation observed, and the coating remained well bonded to the substrate without delamination. When the filler loading was further increased to 25 wt%, the salt spray resistance of the coating decreased slightly, and the corrosion products at the scratch were more than those of the 20 wt% group, but still significantly better than those of the low-content groups and the neat WEP coating.

This macroscopic corrosion inhibition effect at the artificial scratch is highly consistent with the electrochemical test results and XPS interfacial analysis. The significantly suppressed corrosion demonstrates that BTA molecules released from the composite fillers have migrated to the exposed steel surface and formed a dense Fe-BTA chelate passivation film via coordination bonds, which effectively blocks the contact between corrosive media (Cl[−], O₂, H₂O) and the metal substrate and restrains corrosion development at the defect. This active corrosion protection behavior effectively alleviates the protective degradation caused by coating damage and improves the long-term service reliability of the coating system.

It should be noted that the corrosion suppression at the scratch arises from the coupled effect of chemical inhibition and physical barrier. On one hand, BTA molecules released from the functional fillers adsorb onto the exposed metal surface to form a protective chelate film and inhibit the electrochemical corrosion process; on the other hand, accumulated corrosion products and scattered coating debris at the scratch defect act as a physical barrier to slow down further ingress of corrosive media.

The conventional 240 h salt spray test adopted in this work cannot quantitatively decouple the individual contributions of these two mechanisms. In the initial stage of scratch exposure, the active release of BTA inhibitor plays a dominant role in retarding corrosion initiation; with the extension of test time, the physical barrier effect of corrosion product deposition gradually becomes prominent. For this reason, the corrosion suppression behavior observed here is not strictly equivalent to the intrinsic self-healing performance of the coating, and is more accurately defined as a scratch corrosion inhibition effect driven by inhibitor release.

3.6.7. XPS characterization of interfacial passivation film

To elucidate the interfacial corrosion inhibition mechanism of BTA and verify the bonding interaction between inhibitor molecules and the steel substrate, X-ray photoelectron spectroscopy (XPS) was performed on the exposed steel surface within the artificial scratch of the optimal BTA-SiO₂@Al₂O₃-WEP-20 composite coating after 240 h neutral salt spray test. The survey and high-resolution spectra are presented in Fig. 10, where Fig. 10a shows the full survey spectrum and Fig. 10b-e

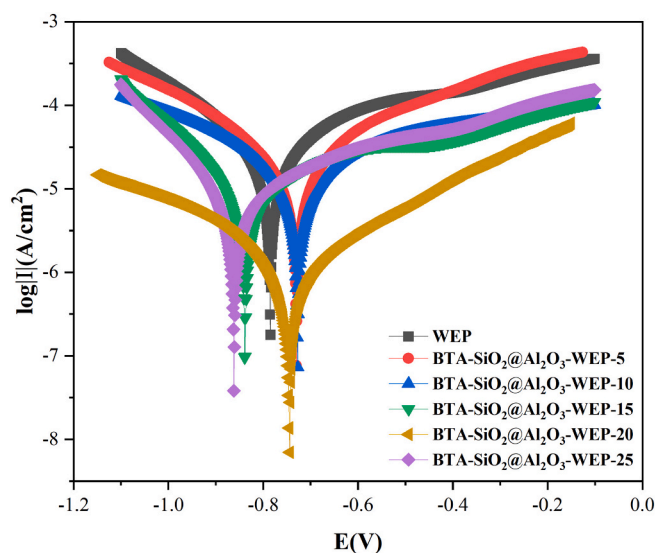


Fig. 9. Potentiodynamic polarization curves of neat WEP and BTA-SiO₂@Al₂O₃-WEP composite coatings with different filler loadings after immersion in 3.5 wt% NaCl solution for 240 h.

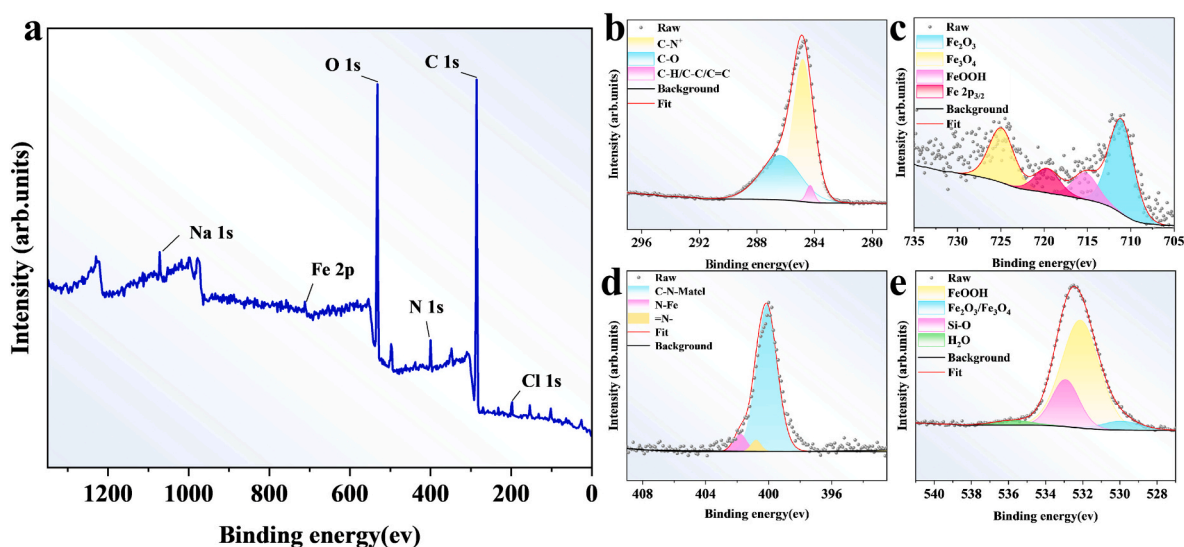


Fig. 10. XPS spectra of the exposed steel substrate surface in the artificial scratch area of BTA-SiO₂@Al₂O₃-WEP-20 composite coating after salt spray accelerated corrosion test (a) XPS survey spectrum; (b) High-resolution C 1 s spectrum; (c) High-resolution Fe 2p spectrum; (d) High-resolution N 1 s spectrum; (e) High-resolution O 1 s spectrum.

display the deconvoluted high-resolution spectra of C 1 s, Fe 2p, N 1 s, and O 1 s, respectively.

The survey spectrum clearly reveals four characteristic elements: C, O, Fe, and N. The detection of N signal is particularly significant, as pristine steel surfaces contain no nitrogen species, providing direct evidence for the successful adsorption of BTA molecules onto the substrate surface. For the C 1 s high-resolution spectrum, three deconvoluted peaks are observed. The dominant peak at 284.8 eV is assigned to C-C/C-H bonds originating from surface adventitious carbon and the benzene ring of BTA. The peak at 286.2 eV corresponds to C-N bonds in the triazole heterocycle of BTA, further confirming the chemical adsorption of BTA molecules. The weak peak at 288.5 eV is attributed to C-O bonds from surface-adsorbed oxygen-containing groups.

In the Fe 2p spectrum, characteristic peaks at 711.0 eV and 724.5 eV are assigned to Fe³⁺ species in Fe₂O₃, with the satellite peak at 719.5 eV corroborating the presence of iron oxides. Notably, no distinct peak corresponding to metallic Fe⁰ (707.0 eV) is detected, indicating that BTA effectively suppressed excessive oxidation of the steel substrate and formed a continuous protective layer at the interface [40].

The N 1 s spectrum is deconvoluted into two distinct peaks. The dominant peak at 400.1 eV is attributed to the neutral triazole nitrogen atoms (=N- and -NH-) in physically adsorbed free BTA molecules, which falls within the widely reported binding energy range of 399.5–400.5 eV for uncoordinated BTA species [41]. The weaker peak at 401.8 eV corresponds to triazole N atoms participating in N → Fe coordination bonds. Compared with free BTA, this peak exhibits a positive shift of approximately 1.7 eV, which arises from the transfer of lone-pair electrons from electron-rich triazole N atoms to the empty orbitals of dissolved Fe²⁺/Fe³⁺ ions. The reduced electron cloud density around the N atoms leads to an increase in the core-level binding energy. This binding energy shift and assignment are in good agreement with previous studies on BTA chemisorption on carbon steel surfaces [40,42].

This result demonstrates that BTA molecules are not only physically adsorbed on the steel surface, but also form stable coordination complexes with iron ions via triazole N active sites. The formed dense and insoluble Fe-BTA chelate passivation film effectively blocks corrosive media from contacting the metal substrate and inhibits the interfacial electrochemical corrosion reactions.

The O 1 s spectrum is resolved into two peaks: the peak at 530.2 eV is assigned to lattice oxygen in Fe₂O₃, while the peak at 531.8 eV corresponds to surface-adsorbed oxygen and hydroxyl groups. These results

collectively indicate that the interfacial protective layer is a composite film consisting of inorganic iron oxides and organic Fe-BTA chelates.

The above XPS analysis results provide direct experimental evidence for the interfacial action mechanism of BTA corrosion inhibitor, which is highly consistent with the results of electrochemical impedance spectroscopy, potentiodynamic polarization curves, and salt spray tests presented earlier. This further confirms the dual synergistic protective effect of “physical barrier + corrosion inhibitor release” of the BTA-SiO₂@Al₂O₃ composite filler.

4. Conclusion

In this work, BTA-SiO₂@Al₂O₃ core-shell structured microspheres were successfully synthesized and incorporated into waterborne epoxy (WEP) matrix to fabricate environmentally friendly anticorrosion coatings with integrated physical barrier and active corrosion inhibition functions. The as-prepared composite fillers exhibited homogeneous dispersion in the WEP matrix due to the strong hydrogen bonding interactions between the silanol groups on the SiO₂ shell and the epoxy resin, which effectively improved the interfacial compatibility and prevented the formation of diffusion pathways for corrosive media. The incorporation of BTA-SiO₂@Al₂O₃ fillers markedly improved the thermal stability and glass transition temperature (T_g) of the WEP coatings, with the T_g increasing from 29.59 °C to 37.9 °C and the initial decomposition temperature elevated by 101.79 °C at 25 wt% filler loading. The corrosion resistance of the composite coatings showed a volcano-type dependence on the filler loading, with the optimal performance achieved at 20 wt% filler content, which possessed a corrosion rate approximately two orders of magnitude lower than that of neat WEP coating and maintained an impedance modulus above 10⁸ Ω·cm² after 240 h of immersion in 3.5 wt% NaCl solution. The 240 h neutral salt spray test further demonstrated that the 20 wt% composite coating could effectively inhibit corrosion propagation at the artificial scratch, showing favorable active protection effect at coating defects, indicating that the composite coating can effectively inhibit corrosion propagation at the artificial scratch. Mechanistically, the superior anticorrosion performance was ascribed to the dual synergistic protection mechanism: the uniformly dispersed core-shell fillers formed a three-dimensional labyrinth network to significantly prolong the diffusion path of corrosive media, while the BTA corrosion inhibitor released from the fillers could chelate with Fe²⁺/Fe³⁺ ions to form a dense passivation film on

the steel substrate surface, as confirmed by XPS analysis. Overall, this study demonstrates that the BTA-SiO₂@Al₂O₃ core-shell composite filler is a promising candidate for reinforcing WEP coatings, and the proposed dual synergistic protection strategy provides a facile and effective approach for the development of high-performance environmentally friendly anticorrosion coatings, with future investigations focusing on optimizing the BTA loading capacity and release kinetics to further enhance the long-term active corrosion protection performance.

The enhancements in thermal stability, mechanical properties and anticorrosion performance are intrinsically correlated, sharing a common microscopic origin from the core-shell structured filler modification. The dense hydrogen-bonding network constructed at the filler-resin interface restricts the thermal motion of epoxy molecular chains, which simultaneously elevates the glass transition temperature, improves coating hardness and reduces the free volume inside the coating matrix. The improved mechanical strength and abrasion resistance help maintain the structural integrity of the coating during service and avoid premature surface defects and microcracks, which in turn prevents corrosive media from penetrating rapidly through damage sites. Furthermore, the densified coating structure not only blocks the penetration of corrosive media and prolongs their diffusion paths, but also reinforces the thermal and mechanical reliability of the whole coating system. This synergistic enhancement of multiple properties endows the composite coating with better comprehensive service performance than single-function modified coatings.

CRedit authorship contribution statement

Qiang Lei: Methodology, Investigation, Data curation, Conceptualization. **Xinyu Wang:** Writing – review & editing, Methodology, Formal analysis. **Zhiguo Xiong:** Resources, Formal analysis. **Runqi Ruan:** Investigation, Data curation. **Xiao Wang:** Visualization, Investigation. **Rulin Li:** Visualization, Data curation. **Yilin Jiang:** Validation, Investigation. **Dongpeng Wang:** Visualization, Validation. **Weilong Shi:** Supervision, Resources. **Weili Li:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

All authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript. No external funding or support from commercial entities was received for this research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2026.110454>.

Data availability

No data was used for the research described in the article.

References

- [1] K. Pieters, T.H. Mekonnen, Progress in waterborne polymer dispersions for coating applications: commercialized systems and new trends, *RSC Sustain.* 2 (2024) 3704–3729.
- [2] Q. Zhu, X. Lei, X. Zha, S. Melhi, J. Ren, B.B. Xu, S. Hao, B. Miao, H. Fu, M.A. Amin, Z.M. El-Bahy, Z. Guo, Polydopamine functionalized Ti3C2 MXene hybrid reinforced waterborne epoxy nanocomposites for enhancing anticorrosion coating application, *Ceram. Int.* 51 (2025) 8832–8842.
- [3] J. Zhang, W.-G. Lu, H. Yan, Z.-B. Zhao, L. Xu, J.-H. Ye, W. Li, Improvement of wear-resistance and anti-corrosion of waterborne epoxy coating by synergistic modification of glass flake with phytic acid and Zn²⁺, *Ceram. Int.* 49 (2023) 17910–17920.
- [4] J.-J. Ju, Z.-B. Zhao, X.-Y. Du, X. Sun, J.-D. Liu, W.-L. Li, Thermally conductive and anti-corrosive epoxy composite coatings by synchronously incorporating boron nitride/graphene fillers and polyvinyl pyrrolidone, *Ceram. Int.* 49 (2023) 28854–28863.
- [5] S. He, C. Zhang, C. Li, Y. Hu, C. Fu, C. Zhang, X. Xu, H. Zhang, Y. He, Enhancement of corrosion resistance and wear resistance of waterborne epoxy resin by polydopamine-modified siloxene, *Ceram. Int.* 51 (2025) 40244–40260.
- [6] Y. Zhan, Y. Chen, H. Dong, Y. Li, A. Sun, X. Chen, X. Yang, F. Zhu, H. Jia, In situ growth of flower-like ZnO onto graphene oxide for the synergistically enhanced anti-corrosion ability of epoxy coating, *Ceram. Int.* 50 (2024) 5914–5926.
- [7] J. Kim, E. Jang, J. Cho, M. Kim, J. Kim, Graphene/SiO₂-reinforced epoxy composite with calcium cross-linking for enhanced thermal conductivity, EMI shielding, and electrical insulation, *Ceram. Int.* 51 (2025) 14444–14454.
- [8] S. Anirudh, K. Aruna Prabha, S. Bhanu Murthy, B. Chennakesava Rao, Enhancement of mechanical properties of matrix by functionalized Multi-Wall Carbon Nanotubes (MWCNT) in composite material, *Mater. Today Proc.* 92 (2023) 1186–1192.
- [9] A.A. Mahuof, A.Y. Qwam Alden, M.H. Mahmood, The synergistic effects of a unique blend of carboxylic acid functionalized multi-walled carbon nanotubes and alkylamine functionalized graphene powder on the strength and stiffness properties of epoxy resins, *Results Mater.* 28 (2025) 100815.
- [10] W. Bunpheng, V.M. Rajavel Muthaiah, S. Ethiraj, S. Singh, R. Dhairiyasamy, C. K. Chan, Surface-state and interphase engineering of ceramic boron carbide-epoxy composites: correlating oxidation, functionalization, and dispersion with mechanical and tribological behavior, *Ceram. Int.* 52 (2026) 5126–5142.
- [11] P. Zhang, X. Zhang, Z. Gao, T. Zhang, S. Hu, Mechanical and bonding behavior of Nano-SiO₂ and epoxy resin reinforced cementitious composite, *J. Build. Eng.* 111 (2025) 113542.
- [12] H. Zeng, M. Bi, Z. Tong, Y. Du, X. Chen, T. Jiang, KH550, KH560, and KH570 modified SiO₂ enhance the moisture resistance, thermal properties and electrical insulation properties of epoxy resin: based on experiments and molecular dynamics simulations, *J. Non Cryst. Solids* 674 (2026) 123922.
- [13] G. Örgen, D. Bayram, Effect of nanoclay on the mechanical and thermal properties of glass fiber-reinforced epoxy composites, *J. Mater. Sci.* 59 (2024) 3467–3487.
- [14] E. Kosedag, R. Ekici, N. Yildiz, U. Caliskan, Effect of SiC and graphene nanoparticles on the mechanical properties of carbon fiber-reinforced epoxy composites, *Polym. Compos.* 44 (2023) 8578–8588.
- [15] G. Karthikeyan, R. Nagarajan, S.O. Ismail, F. Mohammad, K. Krishnan, M.P. Indira Devi, Mechanical and microstructural characterization of graphene dispersed basalt fiber reinforced polymeric composites, *J. Mater. Res. Technol.* 40 (2026) 3422–3435.
- [16] W. Lu, X. Wang, J. Wang, Z. Lin, R. Liu, L. Chen, Z. Li, Z. Zhao, W. Li, Advanced bio-inspired urushiol-modified SiO₂@BN hybrids for enhanced thermal conductivity and superior corrosion resistance in waterborne epoxy coatings, *Prog. Org. Coat.* 211 (2026).
- [17] J. Wang, X. Wang, X. Sun, X. Wang, Q. Li, M. Bu, L. Chen, Z. Zhao, H. Yan, W. Li, Investigate the performance of functional coatings with physically modified boron nitride composite fillers, *Prog. Org. Coat.* 205 (2025).
- [18] X. Wang, W. Li, X. Wang, M. Bu, X. Sun, Z. Zhao, L. Xu, L. Chen, Z. Li, M. Tebyetekerwa, Improved properties of epoxy composite coatings enabled by multi-dimension filler materials, *Prog. Org. Coat.* 197 (2024).
- [19] X. Gong, J. Xu, S. Lv, Preparation and anti-fouling performance of wear-resistant and hydrophobic coating based on epoxy polysiloxane/SiO₂ nanoparticles, *Appl. Surf. Sci.* 744 (2026).
- [20] C. Chen, Y. Xue, X. Li, Y. Wen, J. Liu, Z. Xue, D. Shi, X. Zhou, X. Xie, Y.-W. Mai, High-performance epoxy/binary spherical alumina composite as underfill material for electronic packaging, *Compos. A: Appl. Sci. Manuf.* 118 (2019) 67–74.
- [21] A. Karthik, S. Surendhiran, S. Savitha, K.S.G. Jagan, T.M. Naren Vidarth, R. Senthilmurugan, V. Cheran, Oleic acid tailored Al₂O₃-ZrO₂/epoxy resin coating with enhanced wettability, mechanical property, and controlled surface porosity for anticorrosion applications, *Ceram. Int.* 51 (2025) 40692–40707.
- [22] J. Liu, W. Li, Q. Xu, Y. Zhang, L. Niu, Y. Li, P. Liu, X. Li, Z. Zhang, Fabrication of multiscale alumina nanospheres for improving the thermal conductivity of epoxy resin, *Ceram. Int.* 51 (2025) 8138–8146.
- [23] B. Maloth, V.N. Kumar, Analysis of wear tracks and mechanical properties evaluation of TiO₂ and Al₂O₃ reinforced hybrid epoxy composites, *Mater. Lett.* 398 (2025).
- [24] M.D. Huynh, N.T. Chinh, A.S. Nguyen, N.T. Duong, N.X. Thai, N.V. Giang, T. Hoang, Mechanical, thermal and corrosion-resistant properties of epoxy coatings reinforced with γ-Al₂O₃ modified with titanate coupling agent, *Surf. Coat. Technol.* 531 (2026).
- [25] M. Yang, Y. Gao, M. Imran, W. Wang, J. Li, T. Ren, Quartz sand-based nano-spherical SiO₂ synthesis and its corrosion efficacy of waterborne epoxy resin coatings, *Prog. Org. Coat.* 214 (2026) 110057.
- [26] L. Zhou, X. Wang, X. Zhao, J. Dai, Y. Wang, W. Guo, Z. Li, W. Li, 2-Chloromethylbenzimidazole loaded and polyethyleneimine/poly(sodium-p-styrenesulfonate) decorated fumed silica as filler to prepare pH stimuli-responsive and self-healing epoxy composite coating, *Prog. Org. Coat.* 174 (2023).
- [27] I.I. Udoh, K. Dam-Johansen, Hybrid Zn₃(PO₄)₂/BTA@SiO₂ inhibitive system for synergistic enhancement of active protection in waterborne epoxy coating, *Prog. Org. Coat.* 212 (2026).
- [28] C. Wang, C. Zhao, Y. Li, J. Liu, D. Cheng, T. Shen, J. Zhang, Q. Shen, H. Yang, Composite epoxy coating with dual-responsive Fe₃O₄@BTA-ZIF-8 nanocontainers for active corrosion protection: magnetic field-directed distribution synergized with pH-controlled corrosion inhibitor release, *Prog. Org. Coat.* 209 (2025).
- [29] Y. Zhang, W. Wu, B. Wang, T. Wang, T. Chen, S. Tong, Y. Zhou, Q. Liu, F. Chen, Dual-cation co-precipitated spherical ZP-based pigments: enhancing anticorrosive performance of WEP coatings, *J. Mater. Res. Technol.* 39 (2025) 831–850.

- [30] M. Finšgar, I. Milošev, Inhibition of copper corrosion by 1,2,3-benzotriazole: a review, *Corros. Sci.* 52 (2010) 2737–2749.
- [31] R. Liu, X. Wang, J. Wang, Z. Lin, L. Chen, Z. Li, Z. Zhao, H. Yan, L. Xu, W. Li, Gallic acid-modified montmorillonite reinforced acrylic latex composite coatings: enhanced mechanical and anticorrosion performances via barrier and interface passivation, *Prog. Org. Coat.* 210 (2026) 109649.
- [32] W.-X. Ma, C. Feng, W. Li, X.-Y. Du, J.-D. Liu, Z.-B. Zhao, Insulating electromagnetic-shielding composite coating enables enhanced anti-corrosion and thermal conductivity, *Appl. Surf. Sci.* 744 (2026) 167396.
- [33] P. Li, J. Xiong, Y. Wang, D. Che, X. Liu, S. Zhu, Z. Wang, J. Yang, Preparation and performance of heat-resistant phenolic composites modified with epoxy silicon resin, *Compos. Commun.* 64 (2026) 102808.
- [34] X. Li, C. Xu, Z. Zhang, J. Qiao, A. Ge, H. Wang, P. Shi, Bimodal Al₂O₃-coated TiB₂ powders with enhanced oxidation resistance and sinterability via aluminothermic reduction, *Ceram. Int.* 52 (2026) 35735–35745.
- [35] C. Verma, K.Y. Rhee, A. Alfantazi, Functionalized epoxy resins for enhanced interface properties and corrosion resistance: tailoring of surface and interface properties and performance, *Appl. Surf. Sci. Adv.* 25 (2025) 100685.
- [36] Y. Tang, X. Wu, S. Zou, H. Qin, K. Sun, L. Sun, J. Hou, W. Shi, C. Li, F. Guo, Resorcinol-formaldehyde resin combining epoxy resin as composite coating with efficient anti-corrosion resistance and anti-biofouling capacity, *Prog. Org. Coat.* 203 (2025) 109177.
- [37] X. Fan, Y. Liu, G. Ji, Preparation and long-term corrosion resistance of epoxy resin coatings modified by Fe-Co-Ni-Cr-Ti high-entropy alloy, *RSC Adv.* 16 (2026) 16927–16943.
- [38] L. Zhang, W. Du, Y. Jia, K. Sun, S. Wang, J. Guo, Enhancement of corrosion resistance of waterborne epoxy resin using Ti₃C₂T_x MXene nanosheets modified with l-glutamic acid: preparation, performance and mechanism, *J. Mol. Struct.* 1338 (2025) 142337.
- [39] L. Guo, C. Gu, J. Feng, Y. Guo, Y. Jin, J. Tu, Hydrophobic epoxy resin coating with ionic liquid conversion pretreatment on magnesium alloy for promoting corrosion resistance, *J. Mater. Sci. Technol.* 37 (2020) 9–18.
- [40] W. Zheng, L. Hao, Y. Zhou, B. Gu, Z. Jiang, Y. Fang, Strengthen corrosion resistance of epoxy coating by synergy of oxygen vacancies of CeO₂ nanoparticles as charge capture centers and BTA/TEOS, *Prog. Org. Coat.* 192 (2024) 108481.
- [41] C. Ma, W. Wang, Q. Wang, N. Sun, S. Hu, S. Wei, H. Feng, X. Hao, W. li, D. Kong, S. Wang, S. Chen, Facile synthesis of BTA@NiCo₂O₄ hollow structure for excellent microwave absorption and anticorrosion performance, *J. Colloid Interface Sci.* 594 (2021) 604–620.
- [42] A.N. Synaschyn, V.I. Vyshnevskiy, O.V. Karpenko, I.M. Zin, V.V. Liubchenko, Thin benzotriazole films for inhibition of carbon steel corrosion in neutral electrolytes, *Coatings* 10 (4) (2020) 362.