

Zinc Dimethacrylate/Waterborne Chlorinated Rubber Core–Shell Composite Latexes with Self-Reinforcing, Active Passivation, and Antibacterial Functions for Long-Term Anticorrosion

Haohan Huang, Xiao Wang, Xinyu Wang, Runqi Ruan, Wei Lu, Congcong Zhang, Rulin Li, Qiang Lei, Yilin Jiang, and Weili Li*



Cite This: <https://doi.org/10.1021/acs.langmuir.6c03533>



Read Online

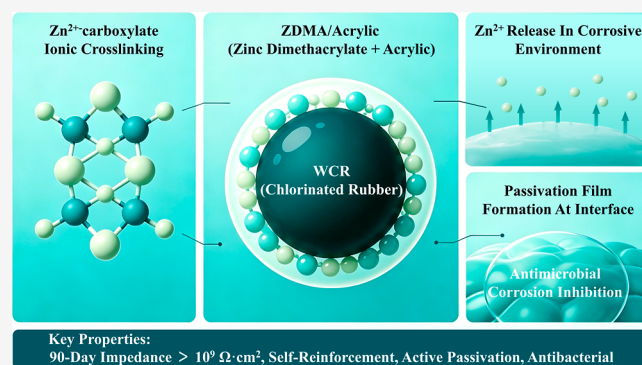
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: A multifunctional waterborne composite coating with self-reinforcing, active passivation, and antibacterial properties was developed by synergistically incorporating zinc dimethacrylate (ZDMA) and waterborne chlorinated rubber (WCR) via semi-continuous seed emulsion polymerization. The core–shell structured ZDMA/WCR latexes combine two synergistic protective mechanisms: bulk self-reinforcing effect via ionic network reconstruction, and interfacial active passivation via Zn^{2+} -derived passivation layers. ZDMA provides ionic cross-linking and controllable Zn^{2+} release, while WCR enhances water resistance and blocks corrosive medium penetration. Electrochemical analysis coupled with distribution of relaxation times (DRT) reveals that the optimized coating retains a low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) above $10^9 \Omega \text{ cm}^2$ after 90 days of immersion, and shows antibacterial activity with the potential to mitigate microbiologically influenced corrosion. The Zn^{2+} -based passivation and dynamic self-renewal mechanism effectively suppresses interface corrosion and coating degradation. This work provides a green, scalable strategy for high-performance waterborne smart anticorrosion coatings used in harsh marine and industrial environments.



1. INTRODUCTION

Metallic corrosion threatens the structural integrity of marine, transportation, and energy infrastructure, causing substantial global economic losses.^{1–3} Organic coatings are the most efficient corrosion mitigation strategy, but conventional solvent-based coatings emit high volatile organic compounds (VOCs), conflicting with strict environmental regulations. Waterborne acrylic coatings are widely investigated eco-friendly alternatives, featuring favorable weatherability, decent film-forming ability and relatively low cost.^{4,5} However, hydrophilic carboxyl and hydroxyl groups (for emulsion stability) inevitably form diffusion pathways for water, oxygen, and chloride ions, increasing water absorption, reducing wet adhesion, and impairing long-term anticorrosion performance.⁶ While molecular design can densify polymer networks, most waterborne acrylic coatings rely on passive physical barriers; microcracks, scratches, or pinholes rapidly induce interfacial corrosion and premature failure.

Chlorinated rubber (CR) has abundant hydrophobic C–Cl bonds and saturated carbon chains, imparting excellent water resistance and barrier properties.^{7–11} Waterborne chlorinated rubber (WCR) enhances acrylic emulsion hydrophobicity and retards electrolyte penetration, but pure WCR-acrylic blends are passive barrier coatings lacking active defect repair, limiting

harsh-environment durability.¹² Smart anticorrosion coatings have shifted to active self-healing/self-reinforcing mechanisms, releasing inhibitors at defects to form passivation layers. Wang et al.¹³ developed a $\text{Cu}_2\text{O}@Ag$ photothermal PDMS self-healing coating (7 cycles, 80 day corrosion resistance via dynamic Cu–N bonds) and applied DRT to analyze corrosion processes, distinguishing bulk charge transport and interfacial charge transfer. Zhou et al.¹⁴ constructed a MoS_2 -modified halloysite-based pH/photothermal dual-responsive system for BTA controlled release; the coating retained $4.35 \times 10^8 \Omega \text{ cm}^2$ impedance after 60 day immersion, and DRT identified four electrochemical processes, providing a model-free failure analysis method.

Zinc dimethacrylate (ZDMA) integrates two protective functions into polymer networks. First, the Zn^{2+} –carboxylate ionic cross-links endow the coating bulk with a self-reinforcing

Received: June 9, 2026

Revised: July 31, 2026

Accepted: August 4, 2026

effect: the dynamic reconstruction of ionic networks and in situ formed zinc-based precipitates can fill internal micropores and restore barrier performance. Second, controlled hydrolysis of ZDMA in corrosive environments releases Zn^{2+} , which migrates to the coating/metal interface and reacts with cathodic OH^- to form insoluble passivation films, realizing interfacial active passivation.¹⁵ This dual-function design overcomes the leaching issue and poor stability of exogenous inhibitors or microcapsules.^{16,17}

Microbiologically influenced corrosion (MIC) accelerates coating degradation and metal damage via biofilms.¹⁸ Zn^{2+} from ZDMA acts as a broad-spectrum antibacterial agent, disrupting bacterial metabolism and DNA replication.^{19–21} The synergy of active Zn^{2+} release and hydrophobic modification enables simultaneous long-term anticorrosion and antibacterial protection, but the synergistic mechanism of ionic cross-linking, Zn^{2+} -mediated passivation, and hydrophobic rubber modification in waterborne acrylic coatings remains largely unexplored.

Electrochemical impedance spectroscopy (EIS) is key for investigating anticorrosion mechanisms, but traditional equivalent circuit fitting relies on a priori system knowledge and cannot resolve overlapping processes in complex coatings.^{22,23} DRT converts frequency-domain impedance to time-domain relaxation spectra, separating polarization processes by characteristic time constants without presupposing circuits.²⁴ Stott et al.²⁵ pioneered DRT for PANI-CNT supercapacitor electrode kinetic analysis, identifying five electrochemical subprocesses and quantifying polarization contributions; the optimized electrode achieved 772 F g^{-1} PANI specific capacitance and 76% rate capability, demonstrating DRT's advantages.

Despite the progress achieved in advanced smart anti-corrosion systems, prevailing strategies still face inherent bottlenecks. Microcapsule- or nanocontainer-loaded inhibitor systems suffer from complicated preparation, poor matrix compatibility and nonrenewable burst release.¹⁴ Dynamic covalent bond-based self-healing coatings generally rely on external stimuli and involve high synthesis costs, and most of them only focus on bulk mechanical repair without active interfacial corrosion inhibition.¹³ Single metal-ion doped systems face the problems of rapid leaching and uncontrollable release rate, leading to unsatisfactory long-term protection performance.¹⁵ Therefore, developing a smart anticorrosion system with simple preparation, spontaneous response, multi-dimensional protection and long-term durability remains an urgent demand.

A multifunctional waterborne composite coating system was designed with ZDMA as a self-renewable Zn^{2+} donor and WCR as a hydrophobic barrier enhancer. ZDMA-X/WCR-Y composite emulsions were synthesized via semicontinuous seed emulsion polymerization, forming WCR-core/ZDMA-modified acrylic-shell particles. ZDMA provides ionic cross-linking, Zn^{2+} -based passivation, and antibacterial functions; WCR enhances hydrophobicity and reduces water absorption. Structure–property relationships were investigated, and the self-reinforcing mechanism was elucidated via EIS, DRT, SKPFM, and SEM-EDS.

This study clarifies the spatiotemporal synergy between bulk self-healing (ZDMA ionic network reconstruction) and interfacial dynamic passivation (Zn^{2+} -based passivation layer growth). The optimized ZDMA-1/WCR-20 coating outperforms pure acrylic coatings in long-term anticorrosion and

antibacterial activity, providing a feasible, eco-friendly, scalable strategy for high-performance waterborne coatings in harsh marine/industrial environments.

2. EXPERIMENTAL SECTION

2.1. Materials

Methyl methacrylate (MMA, chemically pure), styrene (St, chemically pure), 2-ethylhexyl acrylate (2-EHA, chemically pure), 2-hydroxyethyl acrylate (HEA, chemically pure), and Methacrylic acid (MAA, chemically pure) were purchased from Jiangsu Qiangsheng Functional Chemicals Co., Ltd. Zinc dimethacrylate (ZDMA) was supplied by Macklin Biochemical Co., Ltd. (Shanghai). Ammonium persulfate (APS, analytical reagent) was obtained from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Aqueous chlorinated rubber (WCR) was sourced from Ningbo Haoxin Yulong New Material Co., Ltd., while the anionic emulsifier FES32 and nonionic emulsifier S90 were provided by BASF (China) Co., Ltd. and Sasol Chemicals (Shanghai) Co., Ltd., respectively. In addition, Texanol as the film-forming aid (purchased from Macklin) and sodium nitrite (NaNO_2 , analytical reagent) serving as the flash rust inhibitor were acquired from commercial suppliers, together with sodium bicarbonate (NaHCO_3 , analytical reagent) as the pH adjuster from the same source. The bactericide (TS) was supplied by Shanghai Deyude Trade Co., Ltd.

2.2. Synthesis of ZDMA-X/WCR-Y Composite Latex

In this study, a staged variable control strategy was employed to systematically investigate the synergistic regulation mechanism of zinc dimethacrylate (ZDMA) copolymerization (as a self-renewable functional monomer) and waterborne chlorinated rubber (WCR) compounding on the microstructure, self-reinforcement behavior, and long-term protective performance of acrylate latex and its derived composite coatings. Methyl methacrylate (MMA), styrene (St), and 2-ethylhexyl acrylate (2-EHA) were used as base monomers, methacrylic acid (MAA) and hydroxyethyl acrylate (HEA) as hydrophilic functional monomers, and ZDMA (possessing both ionic cross-linking and self-renewable dual properties) as the key functional monomer. The glass transition temperature (T_g) of the acrylate copolymer was designed to be 40°C according to the Fox equation, and the target solid content was set at 40 wt %. Detailed formulation parameters are provided in Table S1 in the Supporting Information.

The core-shell structured acrylate/WCR composite latex was prepared via a semicontinuous seed emulsion polymerization process at a controlled reaction temperature of $80 \pm 1^\circ\text{C}$. Briefly, WCR dispersion, sodium bicarbonate buffer, and 40 wt % of the total deionized water were first introduced into the reaction system as the core seed phase. After stirring and heating to the initiation temperature, the pre-emulsified mixed monomers containing ZDMA and acrylates (premixed with the remaining 60 wt % deionized water and emulsifiers) were uniformly added dropwise into the system at a constant feeding rate over 2.5 h, synchronously with the ammonium persulfate initiator solution. After the dropwise addition was completed, the system was incubated at 80°C for 1.5 h for postpolymerization to reduce residual monomers, then cooled to room temperature and filtered through a 100-mesh sieve to obtain the target product. The as-prepared composite latexes were designated as ZDMA-X/WCR-Y, where X represents the mass fraction of ZDMA relative to the acrylate matrix, and Y represents the mass fraction of WCR relative to the acrylate matrix. The final solid content of all latex samples was controlled at $40 \pm 0.5 \text{ wt } \%$.

To elucidate the optimal synergistic ratio of ZDMA and WCR in the composite acrylate latex system and achieve the synergistic optimization of the self-renewal function and hydrophobic barrier function of the composite coatings, a two-stage variable control experimental design was adopted in this study. In the first stage, the WCR content was fixed at 20 wt % relative to the total mass of the acrylate matrix, and the ZDMA addition amounts relative to the acrylate matrix were set as 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5 wt % in a

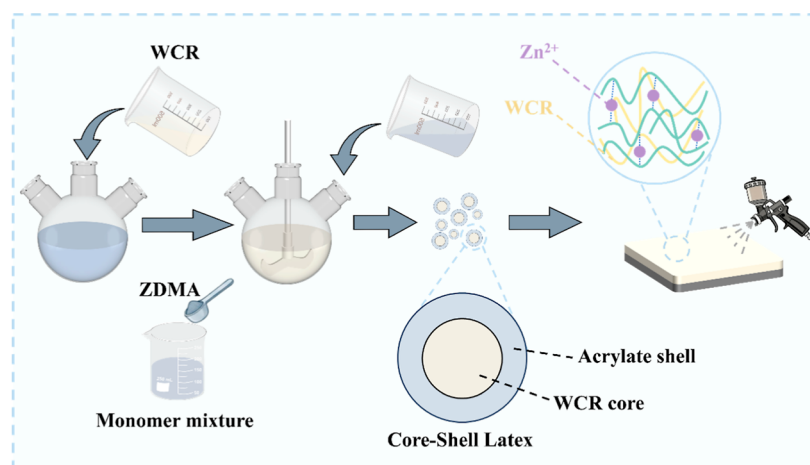


Figure 1. Schematic illustration of the preparation of ZDMA-X/WCR-Y composite coatings.

gradient manner. The regulation effect of ZDMA content on the microstructure and macroscopic properties of the coatings was systematically investigated, with a focus on its influence on the anticorrosion and antibacterial properties. In the second stage, the ZDMA content was fixed at 1.0 wt %, and the mass fractions of WCR based on the total resin solids were adjusted to 0, 10, 20, 30, 40, and 50 wt % in a gradient manner to reveal the synergistic mechanism between the hydrophobic barrier effect of WCR and the self-reinforcement mechanism of ZDMA. In addition, a reference ordinary acrylic latex with the same glass transition temperature was synthesized as the control sample (designated as AL) to systematically investigate the influence of ZDMA and WCR on the properties of the core-shell structured composite latexes and their derived coatings. The detailed formulation parameters of AL are provided in Table S2 in the Supporting Information.

The as-prepared series of composite latexes were mixed with an appropriate amount of film-forming coalescent and stirred until homogeneous. Subsequently, the mixtures were uniformly sprayed onto the surfaces of pretreated mild steel panels and quartz glass substrates. A stepwise heating curing procedure (from room temperature (RT) to 80 °C) was applied to minimize internal defects in the coatings and promote sufficient film formation and cross-linking. Finally, a series of dense and stable ZDMA-X/WCR-Y composite coatings were obtained, which were used for subsequent performance tests and characterizations. The overall preparation process of the ZDMA-X/WCR-Y composite latexes and coatings is schematically illustrated in Figure 1.

2.3. Characterization

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet iS 50 spectrometer (Thermo Fisher Scientific, USA) to analyze the chemical structure of the coatings. The spectra were recorded in the wavenumber range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was carried out on a K-Alpha spectrometer (Thermo Fisher Scientific, USA) to characterize the elemental composition and chemical states of the coating surfaces. The binding energies were calibrated using the C 1s peak at 284.8 eV for charge correction. The particle size distribution of the composite latexes was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS instrument (Malvern, UK). Transmission electron microscopy (TEM) was employed to observe the micromorphology of latex particles using a Tecnai 12 microscope (Philips, Netherlands) at an accelerating voltage of 120 kV. The samples were diluted with deionized water, dropped onto carbon-coated copper grids, and dried at room temperature prior to observation. Field Emission Scanning Electron Microscope (FESEM) was used to examine the surface and cross-sectional morphologies of the coatings with a SEM4000 microscope (CIQTEK Co., Ltd., China) at an accelerating voltage of 5–10 kV. Cross-sectional samples were prepared by cryogenic fracture in liquid nitrogen. Energy-

dispersive X-ray spectroscopy (EDS) was performed using an XFlash 6130 detector (Bruker, Germany) to analyze the elemental distribution in the microregions of the coatings. The pencil hardness of the coatings was determined using a QHQ-A pencil hardness tester (China) in accordance with the GB/T 6739-2006 standard. The coatings' flexibility (minimum bending diameter) was tested with a QTY-32 bending tester (China) following the GB/T 1731-2020 standard. The impact resistance (forward impact) of the coatings was measured using a BGD302 impact tester (China) according to the GB/T 20624.2-2006 standard. The abrasion resistance was evaluated with a JM-V rubber wheel abrasion tester (China) in compliance with the ISO 7784-2:1997 standard, and the mass loss after 500 abrasion cycles was used as the evaluation index. The pull-off adhesion strength of the coatings in the dry state and after immersion in 3.5 wt % NaCl solution for 60 days (wet adhesion) was tested using a PosiTest AT-A adhesion tester (DeFelsko, USA) according to the ASTM D4541 standard. The water contact angle and diiodomethane contact angle of the coating surfaces were measured using a Theta Lite contact angle goniometer (Biolin Scientific, Finland) with a droplet volume of 4 μL . Five different positions were tested for each sample, and the average value was reported. The surface energy (including dispersive component and polar component) of the coatings was calculated using the Owens–Wendt–Rabel–Kaelbe (OWRK) method. The corrosion resistance of the coatings was investigated by electrochemical measurements. A conventional three-electrode system was adopted, with carbon steel as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum sheet electrode ($1 \times 1 \text{ cm}^2$) as the counter electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of 10^5 Hz to 10^{-2} Hz . The EIS data were fitted with equivalent circuits using ZSimpWin software, and model-free analysis was conducted via the distribution of relaxation times (DRT) method on Matlab. All electrochemical measurements were performed on three independently prepared parallel samples, and the EIS measurements for each sample were repeated at least three times. The representative spectra shown in the figures were selected from these repeated measurements, and all exhibited highly consistent features, confirming the reproducibility of the electrochemical data. Scanning Kelvin probe force microscopy (SKPFM, Bruker, Germany) was used to characterize the surface potential distribution of the artificially scratched coatings before and after immersion in 3.5 wt % NaCl solution. The tests were performed at open circuit potential with a probe amplitude of 30 nm and a lift height of 50 μm . The antibacterial performance of the coatings was evaluated by the agar plate diffusion method using “*Escherichia coli*” as the model strain. Coating samples (10 mm in diameter) were placed at the center of agar plates inoculated with bacterial suspension, and incubated at 37 °C for 24 h. The morphology of the inhibition zones was observed and photographed. A blank agar plate was used as the control group,

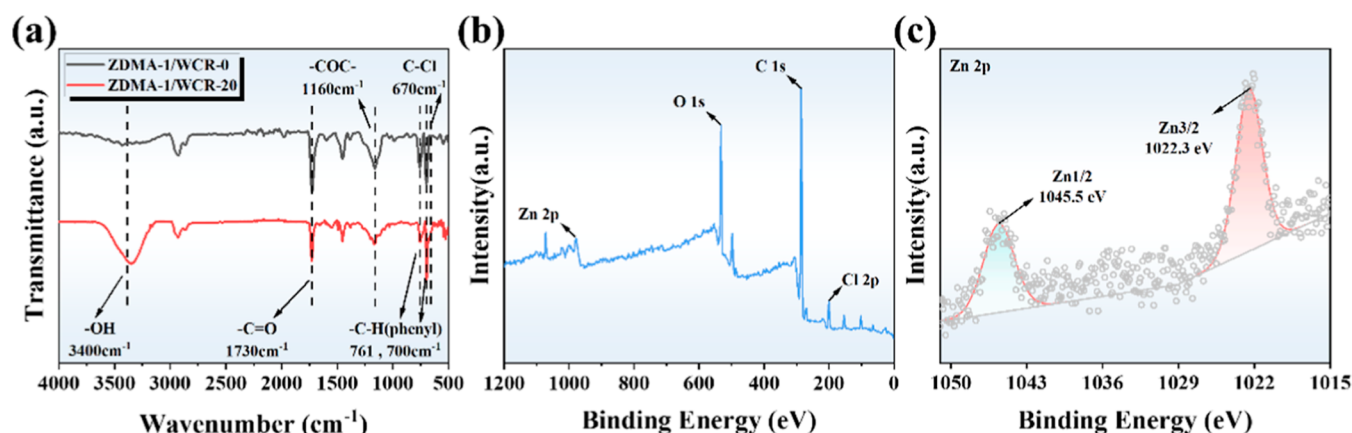


Figure 2. (a) FTIR spectra of ZDMA-1/WCR-0 and ZDMA-1/WCR-20 composite coatings; (b) XPS survey spectrum of ZDMA-1/WCR-20 composite coating; (c) High-resolution Zn 2p XPS spectrum of the same coating.

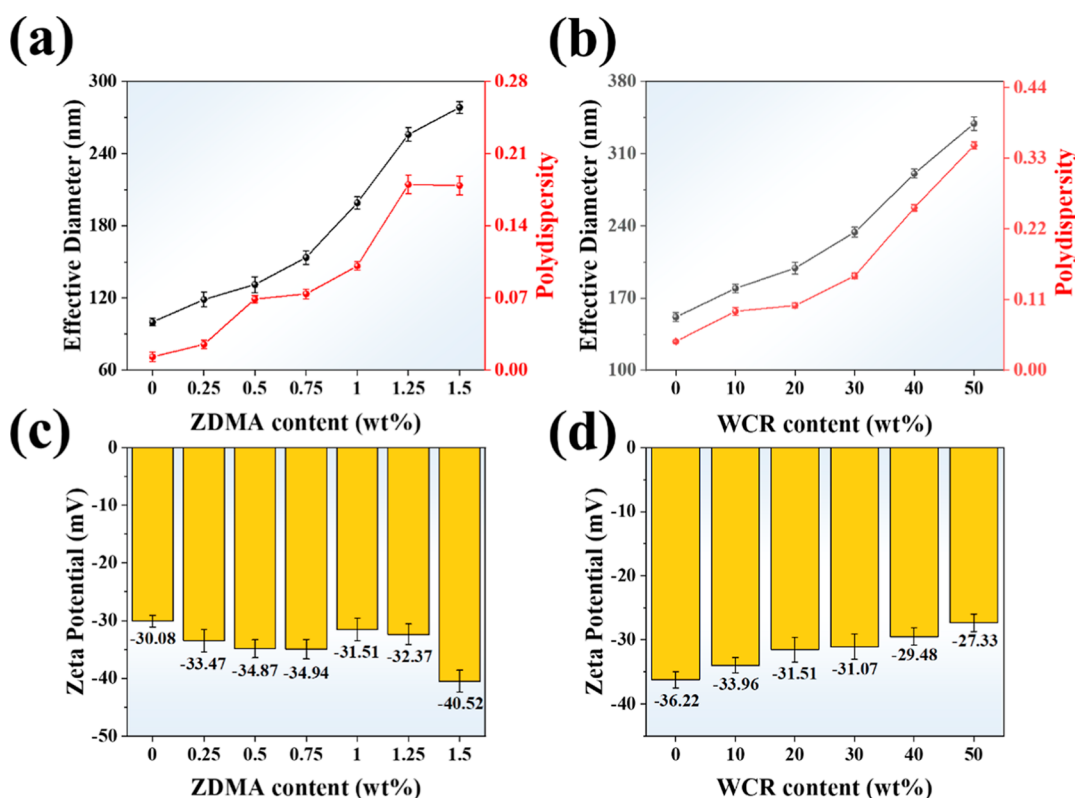


Figure 3. (a) Effective diameter and polydispersity index (PDI) of composite latexes as a function of ZDMA content (WCR fixed at 20 wt %); (b) effective diameter and PDI of composite latexes as a function of WCR content (ZDMA fixed at 1.0 wt %); (c) zeta potential of composite latexes with different ZDMA contents; (d) zeta potential of composite latexes with different WCR contents.

and the bactericide-containing AL coating and ZDMA-1/WCR-20 coating were used as the experimental groups.

3. RESULTS AND DISCUSSION

3.1. Characterization

For the ZDMA-1/WCR-0 sample, after introducing ZDMA into the acrylate latex, the strongest absorption peak in the C–O stretching vibration region exhibited a significant blue-shift relative to the conventional acrylate resin, shifting from ~ 1105 cm⁻¹ to ~ 1160 cm⁻¹. The absorption in this region primarily arises from the C–O stretching vibration of ester bonds (–COOR). This blue-shift indicates that Zn²⁺ ions underwent coordination interactions with the oxygen atoms in the

polymer chains. Such interactions reduced the electron cloud density of the C–O bonds and increased their force constants, thereby elevating the vibration frequency. This spectral behavior not only strongly confirms the successful incorporation of ZDMA into the polymer network but also reveals the ionic coordination interaction mechanism between Zn²⁺ and the ester groups on the polymer side chains, providing direct molecular-level evidence for understanding the microstructure of the composite system (see Figure 2a).

Further comparison of the FTIR spectra of ZDMA-1/WCR-20 and ZDMA-1/WCR-0 shows nearly identical positions of main characteristic absorption peaks, indicating that WCR incorporation does not alter the fundamental chemical

backbone of the acrylate matrix, while a new shoulder peak at 670 cm^{-1} assigned to the stretching vibration of C–Cl bonds in WCR appears in the ZDMA-1/WCR-20 spectrum, which partially overlaps but does not fully degenerate with the out-of-plane bending vibration of phenyl C–H bonds at 700 cm^{-1} to form a characteristic “bulge-like” profile, confirming that WCR is uniformly dispersed in the coating via physical blending or weak intermolecular interactions (hydrophobic interactions, physical entanglement) rather than strong chemical bonding with the acrylate matrix.²⁶

XPS was employed to characterize the surface chemical composition and elemental valence states of the ZDMA-1/WCR-20 composite coating. The survey spectrum (Figure 2b) reveals that the coating surface is mainly composed of C, O, Zn, and Cl elements. Among them, Cl and Zn originate from WCR and ZDMA, respectively, while C and O are derived from the acrylate copolymer backbone, directly confirming the successful incorporation of both ZDMA and WCR into the composite coating system. Peak fitting of the high-resolution Zn 2p spectrum (Figure 2c) shows distinct spin–orbit splitting characteristic peaks at binding energies of 1022.3 and 1045.5 eV, corresponding to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ orbitals, respectively.^{27,28} The energy difference between the two peaks is approximately 23.2 eV, which is consistent with the standard spectral features of Zn^{2+} .²⁹ These results demonstrate that zinc in the system exists stably in the polymer matrix as divalent ions, mainly in the form of hydrolyzable zinc carboxylate structures. Such a chemical structure endows the coating with the ability to release Zn^{2+} responsively in corrosive media.

To reveal the synergistic effects of ZDMA and WCR loadings on the particle size, size distribution, and surface charge characteristics of the composite latexes, a series of samples were systematically characterized by dynamic light scattering (DLS) technique, and the results are shown in Figure 3.

With the WCR content fixed at 20 wt %, the synergistic effects of ZDMA dosage on the particle size, size distribution, and electrostatic stability of the composite latexes were systematically investigated. According to Figure 3a, as the ZDMA dosage increased from 0 to 1.5 wt %, the average particle size of the composite latexes exhibited a continuous increasing trend, rising gradually from 100.1 to 278.3 nm. Specifically, the particle size increased moderately (from 100.1 to 199.1 nm) when the ZDMA content was below 1.0 wt %. However, when the ZDMA content exceeded 1.0 wt %, the particle size increased more rapidly and reached 278.3 nm at 1.5 wt %. This phenomenon can be mainly ascribed to the ionic coordination interactions between Zn^{2+} from ZDMA and the carboxyl/ester groups on the polymer side chains, which form a three-dimensional ionic cross-linking network. The cross-linking structure makes the latex particles more compact and restricts the motion and fusion of polymer chains, thus leading to the increase of particle size. Notably, excessive ZDMA (≥ 1.25 wt %) caused overcross-linking, increased system viscosity, and induced partial particle aggregation, as confirmed by the sharp increase in the polydispersity index (PDI). The PDI increased gradually from 0.013 (0 wt %) to 0.101 (1.0 wt %), and then jumped to 0.180 and 0.179 at 1.25 and 1.5 wt %, respectively, indicating a broader particle size distribution and reduced uniformity at high ZDMA loadings. Zeta potential measurements further revealed the evolution of the electrostatic stability of the system (Figure 3c). When the ZDMA content increased from 0.25 to 0.75 wt %, the absolute

value of the Zeta potential increased slightly from -33.47 mV to -34.94 mV . This is because low-concentration Zn^{2+} coordinates with the surface carboxyl groups without completely neutralizing the negative charges, but instead makes the surface charge distribution more uniform. When the ZDMA content increased to 1.0 and 1.25 wt %, the absolute value of the Zeta potential decreased slightly to -31.51 mV and -32.37 mV , respectively, which is consistent with the double-layer compression effect of divalent cations on anionic emulsions. When the ZDMA content was further increased to 1.5 wt %, the Zeta potential abnormally decreased to -40.52 mV . Combined with the significant increase in PDI of this sample, it is speculated that this phenomenon is related to the uneven surface charge distribution caused by particle aggregation under high cross-linking density, local carboxyl enrichment, or slight pH changes in the test system. Overall, the absolute values of Zeta potential of all samples were greater than 30 mV, indicating that the composite emulsions maintained good electrostatic stability within the experimental range.

Subsequently, with the ZDMA content fixed at 1.0 wt %, the influence of WCR loading on the particle size, size distribution, and surface charge of the composite latexes was systematically investigated (Figure 3b). As the WCR loading increased from 0 to 50 wt %, the average particle size of the composite latexes increased monotonically from 151.7 to 339.0 nm. The particle size increased moderately (from 151.7 to 199.1 nm) when the WCR content was ≤ 20 wt %. However, when the WCR content exceeded 20 wt %, the growth rate of particle size accelerated significantly, reaching 338.9 nm at 50 wt %. This phenomenon is mainly attributed to the hydrophobic WCR being encapsulated inside the latex particles via hydrophobic interactions during emulsion polymerization, resulting in obvious volume expansion of the particles. Meanwhile, the introduction of WCR significantly affected the uniformity of particle size distribution. The PDI increased gradually from 0.045 (0 wt %) to 0.101 (20 wt %), and further rose to 0.147, 0.253, and 0.350 at WCR contents of 30, 40, and 50 wt %, respectively, showing an accelerated increasing trend. These results indicate that when the WCR loading exceeds a critical value (approximately 20 wt %), the excess hydrophobic WCR cannot be effectively stabilized and encapsulated by the acrylate chains, easily forming independent hydrophobic aggregates or causing interparticle bridging, which eventually leads to significant broadening of the particle size distribution and deterioration of the uniformity and stability of the system. The Zeta potential results were highly consistent with the above trends. As the WCR content increased from 0 to 50 wt %, the absolute value of the Zeta potential of the composite latexes decreased monotonically from -36.22 mV to -27.33 mV (Figure 3d). This is because the encapsulation of low-polarity WCR inside the latex particles dilutes the density of carboxyl groups ($-\text{COO}^-$) on the particle surface, leading to a reduction in the total negative surface charge. Nevertheless, the absolute values of Zeta potential of all samples were still greater than 25 mV, indicating that the composite emulsions could maintain basic electrostatic stability even at high WCR loadings without obvious demulsification.

To further verify the particle size and dispersity results obtained from DLS and confirm the core–shell structure of the composite latexes, transmission electron microscopy (TEM) was employed to characterize the morphology of the sample

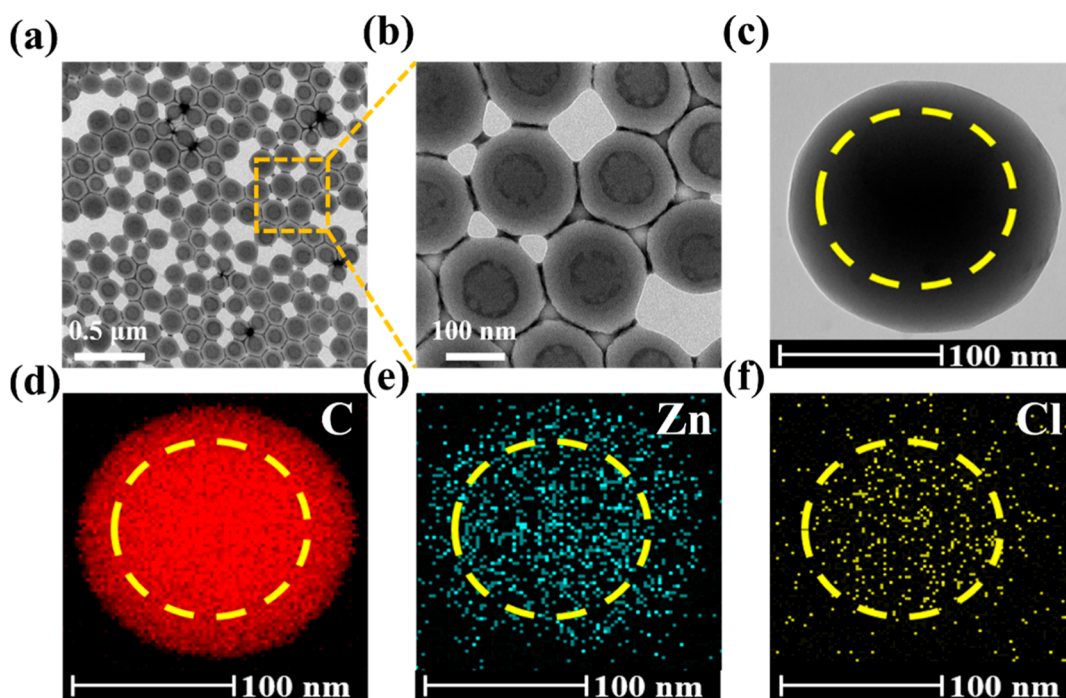


Figure 4. (a) Low-magnification TEM image of ZDMA-1/WCR-20 composite latex particles; (b) high-magnification TEM image of the yellow-boxed region in (a), revealing the distinct core–shell electron contrast; (c) high-resolution TEM image of an individual composite latex particle; (d–f) corresponding TEM-EDS elemental mapping of (d) C, (e) Zn, and (f) Cl for the single particle displayed in (c). The yellow dashed circles in (c–f) denote the boundary of the inner WCR core domain.

prepared with the optimal formulation (ZDMA-1/WCR-20), as shown in Figure 4.

The low-magnification TEM image (Figure 4a) shows that the latex particles exhibit a highly regular spherical morphology, and no irregular, broken, or collapsed particles are observed in the field of view. Statistical analysis of more than 200 particles in the field of view shows that the average diameter of the particles is approximately 195 ± 12 nm, which is in good agreement with the 199.1 nm measured by dynamic light scattering (DLS), verifying the reliability of the particle size data. Meanwhile, the particle size distribution is extremely narrow, consistent with the polydispersity index (PDI = 0.101) measured by DLS, indicating that the polymerization system has excellent particle size controllability and monodispersity. The high-magnification TEM image (Figure 4b) further reveals the fine internal structure of the particles: each latex particle exhibits a clear core–shell double-layer structure. Among them, the core region has a deeper electron contrast, and the shell layer has a lighter electron contrast. The core–shell interface is sharp and clear without a fuzzy transition layer. The core is uniformly located at the geometric center of the particle without eccentricity; the shell thickness is highly consistent, and the deviation of shell thickness between different particles is minimal. This contrast difference originates from the strong electron scattering ability of high-electron-density chlorine atoms in the chlorinated rubber molecular chains, while the relatively low electron density of the acrylate copolymer presents a lighter contrast, together forming a distinct core–shell image with bright and dark regions. In addition, there is no obvious agglomeration or adhesion between the latex particles, and most of the particles are in an independently dispersed state, with only a small amount of slight particle overlap caused by the rupture of the liquid film during TEM sample preparation. The particle surface is smooth and flat

without microscopic defects such as burrs, protrusions, or depressions. This good dispersibility is consistent with the Zeta potential test result (-31.51 mV), and the excellent electrostatic stability ensures that the particles remain independently dispersed in the emulsion. The above characteristics show that the composite latex particles feature narrow size distribution, regular morphology and smooth surface, providing a sound structural basis for dense film formation and reliable protective performance of the derived coatings.

To further corroborate the core–shell architecture and spatial distribution of each component, high-resolution TEM-EDS elemental mapping was conducted on a single ZDMA-1/WCR-20 latex particle (Figure 4c–f), in which the yellow dashed circles denote the inner WCR core boundary. The C and Zn signals uniformly cover the full projected area of the particle, extending across both the core region within the dashed line and the outer shell region (Figure 4d,e), verifying that ZDMA is homogeneously dispersed in the continuous acrylic shell matrix without local agglomeration. In sharp contrast, Cl, the characteristic element of WCR, is highly concentrated inside the dashed core region, with only trace amounts detected in the shell and surrounding background (Figure 4f), demonstrating that the WCR phase is fully encapsulated with negligible diffusion or leakage.

This distinct spatial segregation of characteristic elements directly confirms the WCR-core/ZDMA-acrylic-shell structure, and is highly consistent with the electron contrast in conventional TEM images. The complementary morphological and elemental evidence provides unambiguous support for the well-defined core–shell architecture.

3.2. Structure Morphology and Performance Influencing Factors of ZDMA/WCR Composite Coatings

3.2.1. Surface and Cross-Section Microstructure of Composite Coatings. Based on the optimal emulsion formulation (ZDMA-1/WCR-20) determined previously, the surface and cross-section microstructures of the as-formed composite coating were systematically characterized by FESEM, and the results are shown in Figure 5.

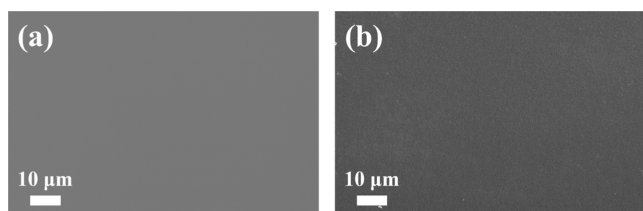


Figure 5. FESEM images of the ZDMA-1/WCR-20 composite coating: (a) surface morphology; (b) cross-section morphology.

As can be seen from the surface morphology (Figure 5a), the coating exhibits a continuous, flat and smooth feature at the micrometer scale without obvious film-forming defects such as cracks, pinholes, local agglomeration or craters. This indicates that the composite latex particles undergo close packing and gradual fusion driven by capillary forces under the synergistic effect of coalescing agents, and achieve sufficient diffusion and entanglement of molecular chains under the staged heating process, finally forming a complete and continuous dense

coating structure. This high surface smoothness reduces the number of adsorption sites for corrosive media and eliminates defect-driven penetration pathways, forming a foundational barrier for the long-term protective performance of the coating.

Observation of the cross-section morphology (Figure 5b) shows that the internal structure of the coating is uniform and dense, and no obvious phase separation, pores or microcracks are observed. The coating is tightly bonded to the metal substrate with a clear and continuous interface, and no interfacial defects such as peeling, gaps or bubbles are found. This excellent dense structure originates from the synergistic effect of two aspects: on the one hand, the three-dimensional ionic cross-linking network introduced by ZDMA significantly enhances the interaction between polymer chains, promotes the segmental rearrangement and tight packing during the film-forming process, and greatly reduces the free volume of the coating; on the other hand, WCR, as the core phase, is preuniformly encapsulated inside the latex particles, and no macroscopic phase separation occurs during the film-forming process. Its hydrophobic molecular chains further fill the gaps in the polymer matrix, further improving the penetration resistance of the coating. The above smooth and dense surface and cross-section structures construct a long-range physical barrier for the penetration of corrosive media such as water, oxygen and chloride ions, which is the core structural basis for the composite coating to achieve excellent long-term corrosion resistance.

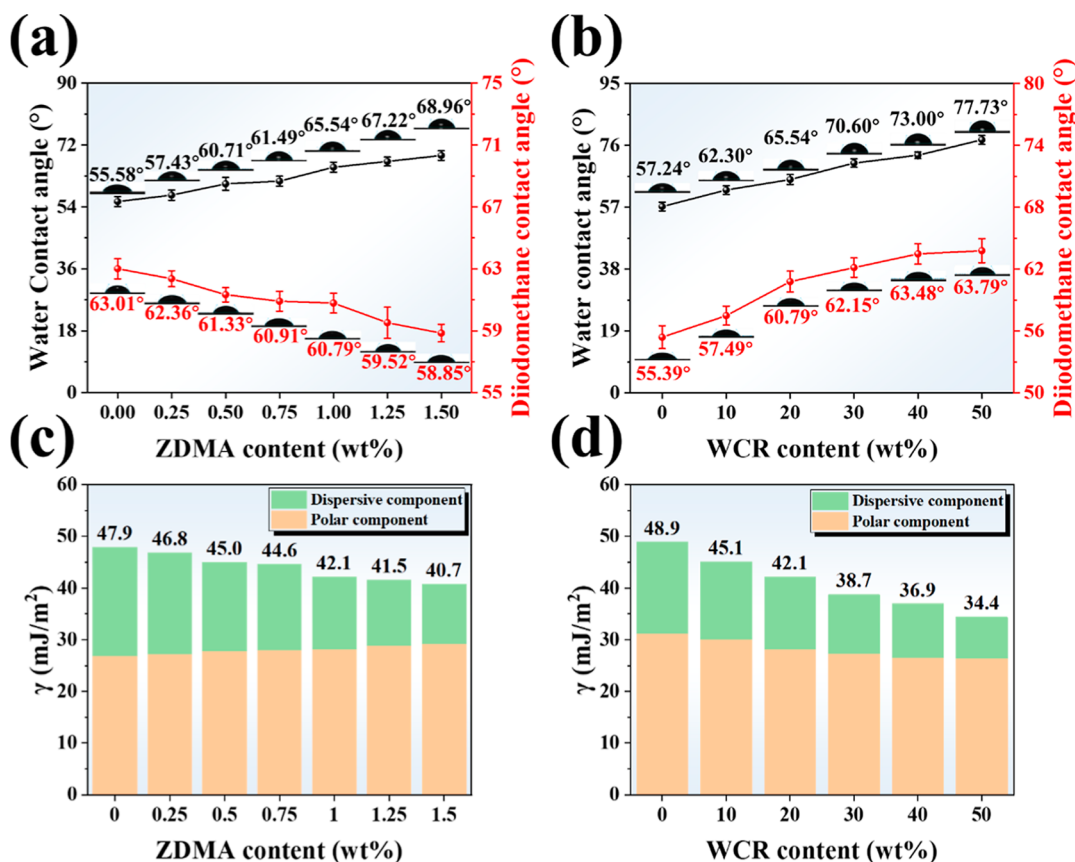


Figure 6. Contact angles of water and diiodomethane and surface energy components of composite coatings as a function of (a,c) ZDMA content (WCR fixed at 20 wt %) and (b,d) WCR content (ZDMA fixed at 1.0 wt %).

3.3. Mechanical Performance of Composite Coatings

Pencil hardness, flexibility, impact resistance, and abrasion resistance are key indicators for evaluating coating service durability, and the synergistic effects of ZDMA and WCR loadings on composite coatings' mechanical and interfacial adhesion properties were investigated, with results in Table S3. With WCR fixed at 20 wt %, pencil hardness increased slightly from B to HB as ZDMA increased (0–1.5 wt %) due to the Zn^{2+} -carboxylate ionic cross-linking network; its limited improvement reflects ionic cross-linking's dynamic reversibility (bond breakage-recombination dissipates stress) and is weaker than covalent cross-linking. Meanwhile, impact resistance increased from 40 to 50 kg cm at ZDMA ≥ 0.5 wt % and stabilized, with all coatings maintaining 0.5 mm flexibility to avoid brittle failure. ZDMA most significantly improved abrasion resistance: compared with pure acrylic coating (AL, wear loss 0.0533 g), 0.25 wt % ZDMA reduced wear loss to 0.0214 g (59.8% reduction), optimal performance was at 0.5 wt % ZDMA (wear loss 0.0102 g, 80.9% improvement), and further ZDMA (0.75–1.5 wt %) slightly increased wear loss (0.0103–0.0129 g) but still far lower than AL due to excessive cross-linking inducing stress concentration. With ZDMA fixed at 1.0 wt %, WCR (0–50 wt %) did not change hardness (HB), impact resistance (50 kg cm), or flexibility (0.5 mm), as it only participates in physical entanglement as a linear non-cross-linked polymer; yet wear loss increased monotonically from 0.0031 to 0.0151 g with WCR due to excessive WCR diluting the ionic network and reducing cohesive strength. Overall, ZDMA optimizes mechanical performance by enhancing abrasion resistance via dynamic ionic cross-linking while maintaining toughness, WCR maintains basic properties but impairs abrasion resistance when excessive, and the optimal formulation is 0.5–1.0 wt % ZDMA and 20 wt % WCR. Dry/wet adhesion determines long-term protective reliability: with WCR fixed at 20 wt %, ZDMA induced a first-increase-then-decrease trend (dry adhesion peaked at 1.28 MPa, 54.2% vs AL; wet adhesion at 0.87 MPa, 770% vs AL), as moderate ZDMA strengthens cohesion and interfacial coordination while excessive ZDMA causes water swelling and reduces wet stability; with ZDMA fixed at 1.0 wt %, WCR (0–50 wt %) monotonically improved dry adhesion (0.96–1.37 MPa) and wet adhesion (0.51–0.86 MPa) due to enhanced physical entanglement, reduced surface energy, and hydrophobic barrier blocking water penetration.

3.4. Surface Wettability and Surface Energy of the Composite Coatings

Surface wettability and surface energy are important parameters for evaluating the performance of composite coatings to interact with aqueous corrosive media. In this study, the contact angles of water and diiodomethane on the coating surface were measured, and the dispersive and polar components of surface energy were calculated by the Owens-Wendt-Rabel-Kaelbe (OWRK) method. The effects of ZDMA content and WCR loading on the surface properties of composite coatings were systematically investigated, and the results are shown in Figure 6.

With the WCR content fixed at 20 wt %, as the ZDMA loading increased from 0 to 1.5 wt %, the water contact angle on the coating surface increased monotonically from 55.58° to 68.96°, while the diiodomethane contact angle decreased gradually from 63.01° to 58.85°. The increase in water contact angle indicates a decrease in the surface hydrophilicity of the

coating, which is closely related to the ionic cross-linking network introduced by ZDMA: the coordination interaction between Zn^{2+} and carboxylate groups can promote the migration of polar groups (e.g., unreacted $-\text{COOH}$, $-\text{OH}$) to the interior of the coating or their participation in cross-linking reactions, thereby reducing the exposure of polar sites on the surface. The decrease in diiodomethane contact angle reflects a slight enhancement of the dispersive force on the coating surface.

The results of surface energy calculation show that with the increase of ZDMA content, the dispersive component of surface energy increased slightly from 27.22 mJ/m² to 29.24 mJ/m², while the polar component decreased significantly from 19.63 mJ/m² to 11.50 mJ/m², leading to a decrease in total surface energy from 46.84 mJ/m² to 40.74 mJ/m². The sharp decrease in the polar component is the main reason for the reduction of total surface energy, which further confirms the “shielding” or “internal migration” effect of ZDMA cross-linking on surface polar groups, thereby weakening the interaction between the coating surface and polar corrosive media.

With the ZDMA content fixed at 1.0 wt %, as the WCR loading increased from 0 to 50 wt %, the water contact angle on the coating surface increased monotonically from 57.24° to 77.73°, and the diiodomethane contact angle increased from 55.39° to 63.79°. The significant increase in water contact angle indicates that the introduction of WCR can greatly improve the surface hydrophobicity of the coating, which is attributed to the enrichment of low surface energy C–Cl bonds and saturated carbon chains in chlorinated rubber molecules on the surface during the film-forming process, forming a dense hydrophobic barrier that effectively inhibits the adsorption of polar media. The increase in diiodomethane contact angle indicates a decrease in the dispersive component on the coating surface.

The results of surface energy calculation indicate that with the increase of WCR content, the dispersive component decreased gradually from 31.22 mJ/m² to 26.40 mJ/m², the polar component decreased sharply from 17.66 mJ/m² to 7.96 mJ/m², and the total surface energy decreased from 48.88 mJ/m² to 34.35 mJ/m². All surface energy components showed a downward trend, and the decrease in the polar component was particularly significant, which is highly consistent with the nonpolar and high hydrophobic characteristics of WCR. When the WCR content reached 50 wt %, the total surface energy of the coating was lower than 35 mJ/m², showing hydrophobic characteristics similar to low surface energy polymers, which can effectively resist the infiltration and penetration of corrosive media.

3.5. Water Absorption and Mass Loss Behavior of the Composite Coatings

The mass variation of coatings exposed to aqueous corrosive media originates from two concurrent processes, namely physical water absorption and swelling as well as dynamic hydrolysis of ionic cross-linking networks. The former characterizes the physical barrier ability and governs the initial permeation rate of corrosive media, while the latter serves as the pivotal mechanism for stimuli-responsive Zn^{2+} release and active anticorrosion protection. Accordingly, exploring the mass evolution behavior at different immersion periods is essential to clarify the anticorrosion mechanism of the as-prepared composite coatings. In this work, the apparent water

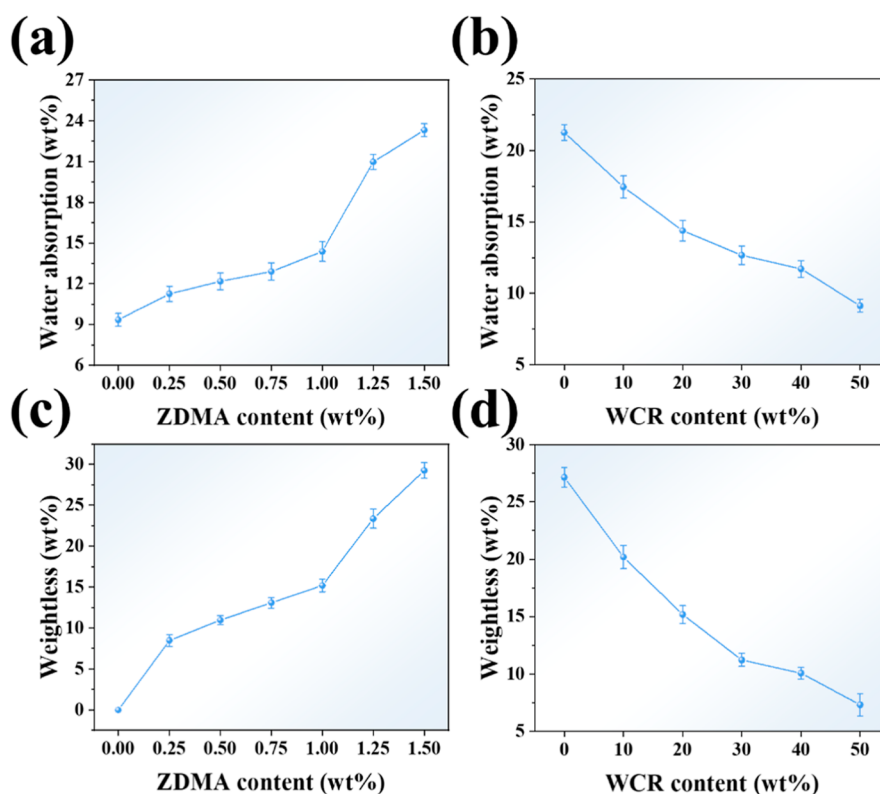


Figure 7. Water absorption and self-renewal mass loss of composite coatings: (a) 7 day water absorption versus ZDMA content; (b) 7 day water absorption versus WCR content; (c) 30 day self-renewal mass loss versus ZDMA content; (d) 30 day self-renewal mass loss versus WCR content.

absorption dominated by physical water uptake after static immersion for 7 days and the mass loss rate mainly caused by ionic cross-link hydrolysis and soluble component dissolution after 30 days of dynamic immersion in flowing 3.5 wt % NaCl solution were systematically measured, and the relevant results are displayed in Figure 7.

With the WCR content fixed at 20 wt %, the 7 day apparent water absorption of the coating increased monotonically from 9.36 to 23.31% as the ZDMA content rose from 0 to 1.5 wt % (Figure 7a). This increase is mainly attributed to the hydrophilicity of the zinc carboxylate groups ($-\text{COO}-\text{Zn}^{2+}$) introduced by ZDMA and the residual hydroxyl groups from the comonomers. These polar groups provide adsorption sites and diffusion channels for water molecules, significantly enhancing the water-absorption capacity of the coating bulk. It should be noted that during the 7 day immersion period, the hydrolysis of Zn^{2+} -carboxylate coordination bonds remains limited, contributing less than 5% to the apparent water absorption. This is because the hydrolysis of zinc carboxylate ionic cross-links is a diffusion-controlled slow process. In neutral 3.5 wt % NaCl solution, water molecules penetrate only 10–20 μm from the coating surface, and only the ionic bonds in this thin surface layer undergo hydrolysis—a conclusion widely supported in similar ionically cross-linked acrylate coating systems.³⁰ Hence, the apparent water absorption at this stage can accurately represent the physical water-absorption characteristics of the coating. With the ZDMA content fixed at 1.0 wt %, after the introduction of hydrophobic WCR, the high-density C–Cl bonds and saturated carbon chains in its molecular chains enrich at the surface during film formation, creating a dense hydrophobic barrier that effectively blocks the penetration pathways of water molecules. As a result, the water

absorption of the coating shows a clear decreasing trend with increasing WCR content (Figure 7b).

With the WCR content fixed at 20 wt %, during the 30 day long-term dynamic immersion, the mass-loss rate of the coating rose sharply with increasing ZDMA content (Figure 7c). This phenomenon is primarily due to the gradual hydrolysis of the zinc carboxylate cross-linked structure: under the continuous attack of Cl^- , the Zn^{2+} -carboxylate coordination bonds cleave, releasing Zn^{2+} from the polymer side chains into the medium. This process is accompanied by the shedding of some uncross-linked oligomers and soluble components generated during network reconstruction, leading to considerable mass loss. With the ZDMA content fixed at 1.0 wt %, the incorporation of WCR suppresses this excessive hydrolysis through a dual mechanism: on the one hand, WCR chains dilute the density of hydrolyzable zinc carboxylate groups per unit volume via physical entanglement; on the other hand, the dense hydrophobic network hinders the penetration of water molecules into the coating interior and the outward diffusion of soluble components, thereby effectively reducing the overall mass-loss rate (Figure 7d). Although linear WCR may undergo slight dissolution during long-term immersion, its dominant role in suppressing the hydrolysis and dissolution of ZDMA is more significant, which helps maintain the long term structural stability of the composite coatings. The composition-dependent and time-accumulated mass loss behavior indirectly reflects the controlled hydrolysis characteristic of the zinc carboxylate network: the release of Zn^{2+} is not a burst process in the initial immersion stage, but a sustained, diffusion-governed process that can be regulated by ZDMA loading and hydrophobic WCR content. This is further corroborated by the continuous

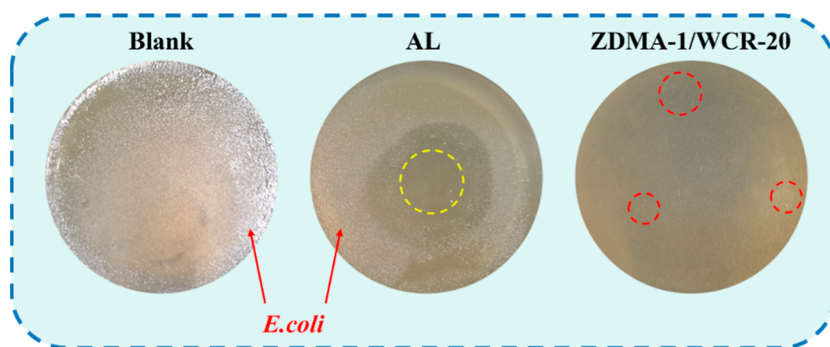


Figure 8. Antibacterial performance of different coatings evaluated by the agar plate inhibition zone method: (a) blank control; (b) AL coating loaded with bactericide; (c) ZDMA-1/WCR-20 composite coating.

increase in charge transfer resistance over 90 days of immersion (Figure 9c), as the sustained supply of Zn^{2+} drives the gradual growth of the interfacial passivation layer.

3.6. Antibacterial Performance and Synergistic Self-Renewal Bacteriostatic Mechanism of ZDMA/WCR Composite Coatings

The antibacterial performance of coatings is of critical importance for inhibiting microbiologically influenced corrosion (MIC), preventing biofilm formation, and extending the service life of coatings.

The ZDMA/WCR composite coatings developed in this work exhibit intrinsic antibacterial activity, which is primarily attributed to the dynamically releasable Zn^{2+} ions from the ZDMA component. Free Zn^{2+} ions can penetrate bacterial cell membranes, specifically bind to thiol groups ($-\text{SH}$) of intracellular proteins, destroy the active centers of key metabolic enzymes, and block energy metabolism pathways. Meanwhile, Zn^{2+} ions can interact with bacterial DNA and interfere with its replication and transcription, thereby effectively inhibiting bacterial growth and reproduction.

From the perspective of microbiologically influenced corrosion (MIC) inhibition, the sustained release of Zn^{2+} acts on multiple stages of the MIC process: it inactivates planktonic bacteria to reduce initial attachment, suppresses extracellular polymeric substance secretion to hinder biofilm maturation, and inhibits corrosive metabolite production by interfering with bacterial metabolic pathways. Combined with the interfacial passivation effect, this multistage action endows the coating with the potential to mitigate MIC. In this work, *E. coli* was used as a model Gram-negative bacterium for preliminary evaluation, and the results provide a reference for the antibacterial performance against marine Gram-negative corrosive microorganisms.²⁰

Notably, owing to the slow hydrolysis characteristic of the zinc carboxylate ionic cross-linking network, Zn^{2+} ions can be released in a sustained and controlled manner in aqueous corrosive media, endowing the coatings with long-term antibacterial capability. This solves the problem of rapid performance degradation encountered in conventional physically doped antibacterial coatings caused by the rapid leaching of antibacterial agents. In this work, *E. coli* was used as a model Gram-negative bacterium, and the antibacterial behavior of coatings with different ZDMA and WCR contents was systematically evaluated by the agar plate inhibition zone method. The results are presented in Figure 8.

The blank control group exhibited uniform and dense bacterial colonies across the entire agar plate with no

discernible inhibition zone, confirming the excellent viability of the bacterial inoculum and the validity of the experimental system. For the AL coating loaded with bactericide, a clear inhibition zone devoid of bacterial growth was observed directly beneath the coating. Surrounding this central zone was a distinct light-colored halo with significantly reduced colony density, while the outermost region showed colony density comparable to that of the blank control. This gradient distribution pattern indicates that the bactericide underwent limited diffusion-controlled release from the coating matrix: the central region had the highest bactericide concentration, sufficient to completely inhibit bacterial growth; the peripheral region had a reduced concentration, resulting in only partial inhibition; and the outermost region was ineffective as the bactericide concentration fell below the minimum inhibitory concentration (MIC). These results confirm that the bactericide was successfully loaded into the coating and possessed certain release capability, but its limited diffusion range precluded long-term and broad-spectrum antibacterial efficacy.

In contrast, the ZDMA-1/WCR-20 coating showed substantially higher antibacterial activity than the AL control coating. Virtually no bacterial colonies were observed on the agar plate, with only a few isolated colonies present. This superior antibacterial effect originates from the synergistic action between Zn^{2+} ions and the bactericide. On one hand, the sustained release of bactericide from the coating disrupts the structural integrity of bacterial cell membranes. On the other hand, Zn^{2+} ions released via hydrolysis of ZDMA possess intrinsic auxiliary antibacterial activity, which can interfere with bacterial enzymatic systems and promote the generation of intracellular reactive oxygen species (ROS). More importantly, the dynamic self-renewal property of ZDMA in this coating system facilitates the continuous migration of bactericide from the coating interior to the surface, overcoming the limitation of solely passive diffusion in conventional acrylic coatings and achieving long-term, broad-spectrum antibacterial efficacy. The presence of these sporadic colonies may be attributed to extremely minor microdefects on the coating surface or accidental contamination during sample preparation, which does not compromise the overall excellent antibacterial performance of the coating.

3.7. Electrochemical Performance Analysis of ZDMA/WCR Composite Coatings

EIS serves as a primary nondestructive method for evaluating anticorrosion performance of organic coatings, offering quantitative information on barrier properties and interfacial

corrosion kinetics.^{31–33} However, conventional equivalent circuit fitting is limited by subjectivity and nonuniqueness, especially in complex composite systems with overlapping electrochemical processes. The distribution of relaxation times (DRT) provides a model-free approach to distinguish polarization processes by characteristic time constants without prior circuit assumptions, and has been widely used to analyze failure and self-healing dynamics of smart anticorrosion coatings.^{14,34,35} In this work, DRT combined with equivalent circuit fitting was employed to trace the electrochemical evolution of ZDMA/WCR coatings immersed in 3.5 wt % NaCl solution. Quantitative analysis of DRT peak positions, areas, and temporal evolutions reveals the kinetics of coating degradation, ionic cross-link hydrolysis, Zn^{2+} inhibition, and self-renewal repair, offering direct electrochemical evidence for the long-term protection mechanism of the composite coatings.

First, to investigate the effect of ZDMA content on the anticorrosion performance of the composite coating system, the relative mass fraction of WCR was first fixed at 20 wt %, and the ZDMA content was systematically varied from 0.25 to 1.5 wt % in the electrochemical analysis (Figure S1).

3.7.1. Nyquist Plot Analysis. The diameter of the capacitive arc in Nyquist plots directly reflects coating resistance, serving as the core indicator for evaluating barrier performance.³⁶ All coatings exhibited initial capacitive arc diameters $>10^9 \Omega \text{ cm}^2$, indicating dense and defect-free structures. The pure AL coating showed the optimal initial barrier performance due to the lowest content of hydrophilic functional groups. Introduction of ZDMA slightly reduced the capacitive arc diameter by increasing coating polarity, while the hydrophobic effect of WCR partially offset this adverse impact, maintaining initial impedance above $10^9 \Omega \text{ cm}^2$.

During the middle immersion period (7–30 days), only the AL coating showed decreased impedance, while all composite coatings exhibited abnormal impedance increase. This was attributed to the self-reinforcement mechanism of ZDMA: water penetration triggered ZDMA hydrolysis to release Zn^{2+} , which formed an insoluble passivation layer at the coating/metal interface, blocking micropores and creating a chemical barrier. After 60 days, the impedance of AL decreased to $\sim 10^7 \Omega \text{ cm}^2$, and samples with low ZDMA content ($<1 \text{ wt } \%$) also began to show slow impedance attenuation.

At day 90, the impedance of AL dropped to $\sim 10^5 \Omega \text{ cm}^2$, indicating almost complete failure. Samples with low ZDMA content still maintained relatively high impedance, while those with excessive ZDMA ($>1 \text{ wt } \%$) showed decreased impedance due to excessive water absorption and swelling that destroyed the self-reinforcement network. ZDMA-1/WCR-20 achieved the optimal balance between hydrophilicity and hydrophobicity, exhibiting the best long-term protective performance.

3.7.2. Bode Impedance Plot Analysis. The impedance modulus at low frequency (0.01 Hz) is a key quantitative indicator for evaluating long-term coating protection.³⁷ All coatings showed initial low-frequency impedance $>10^9 \Omega \text{ cm}^2$, consistent with Nyquist plot results. After 90 days of immersion, the low-frequency impedance of AL decreased to $10^5 \Omega \text{ cm}^2$, while composite coatings remained at $>10^9 \Omega \text{ cm}^2$, directly confirming the self-reinforcement effect of the passivation layer and exposing the inherent defects of linear non-cross-linked structures.

3.7.3. Bode Phase Angle Plot Analysis. The height and width of the phase angle plateau intuitively reflect coating compactness. Initially, all samples had wide phase angle plateaus near -90° , with ZDMA-1.5/WCR-20 showing the narrowest plateau due to excessive hydrophilic groups. With prolonged immersion, only the AL coating showed gradually decreasing phase angles and shrinking plateaus, indicating the formation of ion penetration channels.

A second phase angle peak appeared in the intermediate frequency region (10^0 – 10^3 Hz) for composite coatings, corresponding to the establishment of the interfacial passivation layer. This peak never dropped below -45° , indicating no significant corrosion reaction occurred. At the late corrosion stage, the phase angle of AL approached 0° , showing pure resistive characteristics and complete failure, while composite coatings had phase angles of $\sim -20^\circ$ due to increased dielectric constant from water absorption, with the metal substrate still effectively protected by the passivation layer.

3.7.4. DRT Spectrum Analysis. Converting EIS data into a distribution of relaxation times (DRT) spectrum with $\log(\tau)$ as the abscissa can resolve different polarization processes that may exist in the system (such as coating bulk response, interfacial reactions, etc.). The number of peaks in the spectrum indicates the number of time constants in the system, the abscissa $\log(\tau)$ corresponds to the characteristic relaxation time of each process, and the peak area reflects the contribution weight of that process to the total impedance.

For the AL coating, its DRT spectrum always presented two clearly distinguishable peaks throughout the 90 day immersion process. The high-frequency peak (smaller $\log(\tau)$) corresponded to the dielectric response of the coating bulk ($\tau = \text{RcCc}$), and the low-frequency peak (larger $\log(\tau)$) was attributed to the electrochemical reaction process at the coating/metal interface ($\tau = \text{RctCdI}$). This indicated that due to its linear non-cross-linked structure and poor barrier performance, the electrolyte had penetrated to the metal interface and initiated interfacial corrosion reactions at the early stage of immersion, thus showing a bimodal feature from the beginning. It is worth noting that the $\log(\tau)$ positions of the two peaks did not shift significantly to the left with immersion time. With the extension of immersion time, the accumulation of interfacial corrosion products (such as Fe oxides/hydroxides) may keep the relaxation time of the interfacial process stable or even slightly shift to the right. This phenomenon further confirmed that once the AL coating failed, its interfacial electrochemical behavior tended to be stable.

Unlike AL, the composite coatings only presented a single high-frequency peak at the initial stage of immersion (day 1), corresponding to the complete coating bulk response, indicating that the electrolyte had not penetrated the coating to reach the metal interface, which was attributed to the barrier effect of WCR hindering the penetration of corrosive media. However, when the ZDMA content was $\geq 1 \text{ wt } \%$, two peaks appeared on day 1 due to the increased content of hydrophilic groups. With the extension of immersion time (about 7 days later), the DRT spectrum gradually evolved into a bimodal pattern: the high-frequency peak ($\log(\tau) > 1$) still belonged to the coating bulk, and the low-frequency peak ($\log(\tau) < 1$) corresponded to the newly established interfacial process, i.e., the passivation layer formed by the reaction of Zn^{2+} released from ZDMA hydrolysis with cathodic OH^- . The $\log(\tau)$ of this

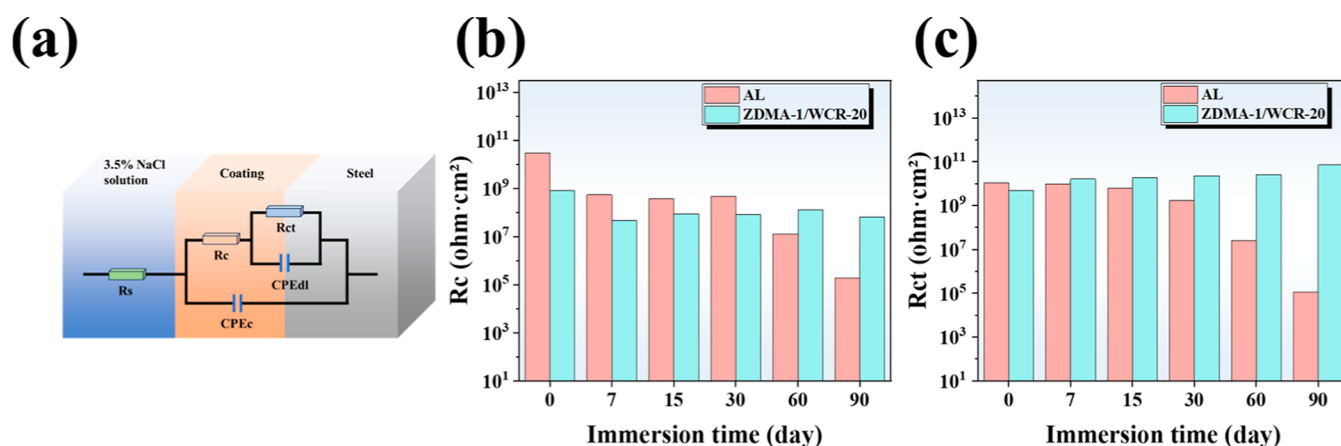


Figure 9. (a) Schematic illustration of the two-time-constant equivalent circuit model employed for fitting electrochemical impedance spectroscopy (EIS) data; (b) evolution of coating resistance (R_c) and (c) charge transfer resistance (R_{ct}) for pure acrylic coating (AL) and optimal ZDMA/WCR composite coating (ZDMA-1/WCR-20) during immersion in 3.5 wt % NaCl solution for 90 days.

low-frequency peak continued to shift to the right with immersion time, indicating an increase in interfacial relaxation time, which directly reflected the gradual densification of the passivation layer and the continuous rise in charge transfer resistance (R_{ct}). Meanwhile, the relative area of the low-frequency peak gradually increased while the area of the high-frequency peak decreased accordingly, indicating that the contribution weight of the interfacial process to the total impedance was continuously increasing. Since the passivation layer effectively inhibited the corrosion reaction, the total impedance still showed an upward trend. This bimodal evolution law was in sharp contrast to the always bimodal and no significant left shift characteristics of the AL coating, highlighting the active regulation effect of the self-reinforcement mechanism on the interfacial process.

Next, to investigate the effect of WCR content on the anticorrosion performance of composite coatings, the ZDMA content was fixed at 1 wt %, and the WCR mass fraction was adjusted from 0 to 50 wt %. Figure S2 presents the EIS and DRT spectra of the corresponding coatings during immersion in 3.5 wt % NaCl solution.

All coatings exhibited an initial capacitive arc diameter $>10^9 \Omega \text{ cm}^2$, indicating dense and defect-free initial structures. With increasing WCR content, the initial capacitive arc diameter first increased and then stabilized. For the coating with WCR = 0 wt % (ZDMA-1/WCR-0), the arc shrank significantly after 90 days, with impedance decreasing to $\sim 10^7 \Omega \text{ cm}^2$, reflecting insufficient hydrophobic barrier performance. Coatings with WCR = 10–20 wt % showed a pronounced increase in capacitive arc diameter during the middle immersion period (7–30 days), attributed to the synergistic effect of WCR's hydrophobic barrier and ZDMA's self-reinforcement mechanism. The optimal stability was achieved at WCR = 20 wt %, maintaining impedance $>10^9 \Omega \text{ cm}^2$ after 90 days. Excessively high WCR content (>30 wt %) led to accelerated impedance decay in the late stage due to increased brittleness and interfacial defects.

Bode plots showed that coatings with WCR = 10–20 wt % retained low-frequency impedance $>10^9 \Omega \text{ cm}^2$ after 90 days, while the WCR = 0 wt % coating dropped to $\sim 10^7 \Omega \text{ cm}^2$. The high-frequency phase angle plateau remained near -90° for WCR-containing coatings, with only a weak second phase

angle peak in the intermediate frequency region, indicating effective inhibition of interfacial corrosion reactions.

DRT spectra revealed that the WCR = 0 wt % coating showed bimodal features from the initial stage, with the low-frequency peak (interfacial corrosion) dominating impedance decay. In contrast, coatings with WCR = 10–20 wt % exhibited only a single high-frequency peak initially, followed by the gradual emergence of a low-frequency peak corresponding to the passivation layer formed by $\text{Zn}^{2+}-\text{OH}^-$ reactions. The low-frequency peak continuously shifted rightward with increasing area, reflecting progressive densification of the passivation layer. Excess WCR led to early appearance of the low-frequency peak and reduced peak shift amplitude, indicating impaired self-reinforcement due to interfacial defects.

In summary, WCR's hydrophobic barrier effect delays corrosive medium penetration, providing a critical time window for ZDMA hydrolysis and passivation layer formation. The optimal synergistic balance is achieved at 20 wt % WCR, maximizing long-term anticorrosion performance.

To fully exploit the model-free analytical capability of DRT, we quantitatively deconvoluted the DRT spectra of all formulations and clarified the physical attribution of each relaxation process. Two characteristic relaxation peaks can be distinguished in all samples: the high-frequency peak ($\tau \approx 10^{-5}-10^{-1} \text{ s}$) corresponds to the bulk coating relaxation process associated with R_c and coating capacitance, while the low-frequency peak ($\tau \approx 10^1-10^3 \text{ s}$) is attributed to the interfacial charge transfer relaxation process associated with R_{ct} and double-layer capacitance.

Quantitative cross-comparison across all formulations reveals consistent composition-dependent trends. For the high-frequency peak, increasing WCR content reduces peak intensity and shifts the characteristic relaxation time to longer time scales, verifying the enhanced barrier effect of the hydrophobic WCR phase. After 90 days of immersion, the high-frequency peak area of pure AL decreases from 3.10×10^8 to 2.06×10^6 (a reduction of 99.3%), indicating nearly complete barrier failure, whereas that of ZDMA-1/WCR-20 increases from 1.67×10^9 to 2.53×10^9 (an increase of 51.7%), confirming the bulk self-reinforcing effect from a model-free perspective. For the low-frequency peak, increasing ZDMA content reduces peak intensity and shifts the relaxation time to longer time scales, reflecting improved interfacial corrosion

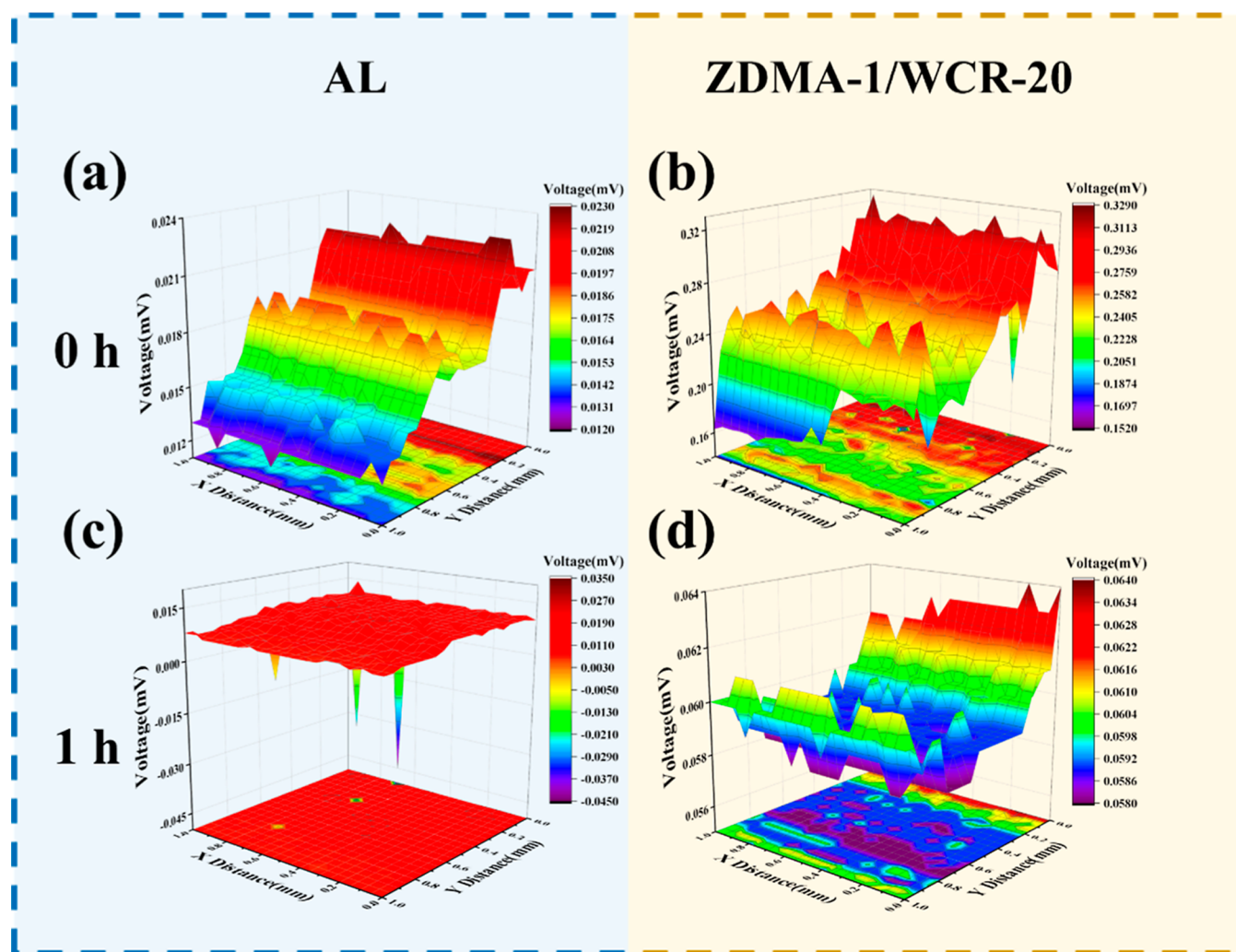


Figure 10. Surface potential distribution of artificially scratched AL and ZDMA-1/WCR-20 coatings characterized by Scanning Kelvin Probe Force Microscopy (SKPFM) before and after immersion in 3.5 wt % NaCl solution for 1 h.

inhibition. After 90 days of immersion, the low-frequency peak area of ZDMA-1/WCR-20 increases from 2.55×10^9 to 1.49×10^{10} (an increase of 4.8-fold), directly demonstrating the continuous growth of the zinc-based passivation layer; in contrast, the low-frequency peak area of pure AL plummets from 1.14×10^9 to 1.06×10^6 (a reduction of 99.9%), reflecting catastrophic interfacial corrosion. Model-free DRT analysis further confirms that the synergistic system achieves dual enhancement of bulk barrier performance and interfacial corrosion resistance, providing reliable electrochemical evidence for the self-reinforcing and active passivation mechanism. The detailed quantitative DRT parameters for all formulations at each immersion time point are summarized in Tables S4 and S5 in the Supporting Information.

The corrosion protection and failure behaviors of pure acrylic (AL) and optimized ZDMA-1/WCR-20 composite coatings were quantitatively explored via equivalent circuit fitting of EIS data during 90 day immersion in 3.5 wt % NaCl solution. A two-time-constant equivalent circuit (Figure 9a) was adopted, including solution resistance (R_s), coating bulk resistance (R_c), coating constant phase element (CPE_c), charge transfer resistance (R_{ct}), and double-layer constant phase element (CPE_{dl}). The dynamic evolution of R_c and R_{ct} was used to distinguish the contributions of coating barrier

performance and interfacial passivation to the overall anticorrosion capability.^{38,39}

The R_c value, representing coating compactness and ion transport resistance, exhibited entirely different evolution trends for the two coatings (Figure 9b). The linear non-cross-linked AL coating displayed a monotonic exponential decay in R_c , decreasing from an initial $3.02 \times 10^{10} \Omega \text{ cm}^2$ to below $1.91 \times 10^5 \Omega \text{ cm}^2$ after 90 days. This irreversible degradation originated from water-induced polymer chain plasticization and the formation of continuous ion permeation channels by inherent hydrophilic groups, continuously weakening the coating barrier effect. In contrast, ZDMA-1/WCR-20 presented a distinctive decrease-then-increase self-reinforcing profile. The initial slight decline of R_c (from 8.03×10^8 to $4.61 \times 10^7 \Omega \text{ cm}^2$ within 7 days) resulted from the hydration of ionic cross-linking sites. Subsequent Zn^{2+} released from ZDMA hydrolysis reacted with cathodic OH^- to form insoluble zinc-based nanoprecipitates, which blocked internal micropores and restored the ionic cross-linking network, gradually recovering R_c to $6.63 \times 10^7 \Omega \text{ cm}^2$ at the end of immersion. This phenomenon confirms that corrosive medium infiltration can serve as a driving force for the spontaneous densification of the composite coating network.

The R_{ct} evolution, a critical indicator of interfacial electrochemical reactivity and passivation layer integrity, further verified the distinct protective mechanisms (Figure 9c). AL coating suffered severe interfacial corrosion, with R_{ct} plummeting from 1.05×10^{10} to below $1.13 \times 10^5 \Omega \text{ cm}^2$, as the failed coating allowed rapid penetration of Cl^- and O_2 to accelerate substrate anodic dissolution and cathodic reactions. Conversely, ZDMA-1/WCR-20 exhibited a continuous monotonic increase in R_{ct} , rising from 4.68×10^9 to $7.09 \times 10^{10} \Omega \text{ cm}^2$ over 90 days. The gradually accumulated and densified zinc-containing passivation layer initially hindered electron transfer, subsequently thickened and transformed into stable basic zinc salts in chloride media. The recovered coating barrier further reduced electrolyte supply, maintaining the interface in an electrochemical quiescent state and suppressing interfacial corrosion persistently.

Based on the R_c evolution, the bulk barrier self-healing efficiency is calculated using the minimum R_c at day 7 as the damaged baseline. The barrier property recovers by $\sim 43.8\%$ at day 90 relative to the lowest value, verifying the micropore-filling effect of zinc-based precipitates. Meanwhile, the R_{ct} increases by 15.1 times over 90 days of immersion, reflecting the continuous growth and densification of the interfacial passivation layer. Compared with the pure AL coating, the interfacial corrosion inhibition efficiency of the composite coating exceeds 99.9% at day 90.

To quantitatively decouple the contributions of bulk self-reinforcing and interfacial active passivation, we analyzed the evolution of R_c and R_{ct} following the impedance-based decoupling framework for multimechanism anticorrosion coatings reported in previous work.⁴⁰

The bulk self-reinforcing effect achieves a 43.8% barrier recovery at day 90 relative to the minimum R_c value at day 7, and maintains the coating resistance over 340 times higher than that of the pure acrylic coating after 90 days of immersion. The interfacial active passivation effect dominates the total protective performance, delivering a 15.1-fold increase in R_{ct} and an interfacial corrosion inhibition efficiency over 99.9% compared with the control.

The two effects form a spatiotemporal synergistic system during long-term immersion. In the initial 7 days (induction stage), water penetration triggers initial hydrolysis of zinc carboxylate bonds; the bulk barrier temporarily decreases, while a small amount of released Zn^{2+} initiates interfacial passivation. From day 7 to day 90 (synergistic enhancement stage), the bulk ionic network acts as a controlled-release Zn^{2+} reservoir to sustain long-term interfacial passivation, while the interfacial passivation layer in turn inhibits coating delamination and maintains matrix integrity, forming a positive protective feedback loop.

Comparative analysis demonstrated a vicious degradation cycle for AL, where synchronous attenuation of R_c and R_{ct} mutually accelerated coating deterioration and interfacial corrosion. For ZDMA/WCR composite coating, the asynchronous evolution of R_c and R_{ct} achieved favorable spatiotemporal synergy: interfacial passivation initiated in the early immersion stage, followed by coating self-healing to further block ion channels and form a positive protective feedback loop. The improved low-frequency impedance modulus macroscopically reflected the simultaneous enhancement of coating barrier and interfacial protection. Overall, the excellent long-term anticorrosion performance of ZDMA-1/WCR-20 originated from the synergistic effect between coating bulk self-healing and

dynamic interfacial passivation, which converted corrosion infiltration into a driving force for persistent protective structure densification.

To further unravel the anticorrosion mechanism of the composite coatings, Scanning Kelvin Probe Force Microscopy (SKPFM) was employed to characterize the surface potential distribution of artificially scratched coatings before and after immersion in 3.5 wt % NaCl solution.⁴¹ AL and ZDMA-1/WCR-20 composite coating were selected as test samples, with potential images recorded at the initial state and after 1 h of immersion, respectively; the results are presented in Figure 10.

At the initial state, distinct potential differences were observed in the scratched regions of both coatings. In the intact coating areas, the potential was high and uniformly distributed; in contrast, the potential at the scratches (damaged areas) decreased significantly, indicating that the scratches directly exposed the metal substrate, allowing corrosive media to quickly contact the bare metal surface. This phenomenon confirms the validity of the scratch test, as both coatings exhibited local defects at the initial stage, with the substrate metal at the scratches in a thermodynamically unstable state.

After 1 h of immersion, the surface potential of the AL coating underwent a dramatic evolution. The potential across the entire scanning area generally decreased to near 0 V (relative to the reference electrode), and three distinct low-potential points (negative potential peaks) appeared near the scratches. This indicates that under the continuous action of corrosive media, electrolytes rapidly penetrated from the scratch defects to the coating/metal interface, triggering local corrosion reactions. The emergence of low-potential points corresponds to the initiation of pitting corrosion; with prolonged immersion, these pits may gradually expand and merge, leading to large-area cathodic delamination of the coating and accelerated corrosion of the substrate metal. This behavior is consistent with the rapid barrier failure induced by the linear non-cross-linked structure of the AL coating.

In striking contrast, although the overall potential of the ZDMA-1/WCR-20 composite coating also decreased after 1 h of immersion, a clear high-low potential distribution was still maintained. The low-potential regions were mainly confined to the vicinity of the original scratches and did not extend to the surrounding intact coating areas; the potential of the intact coating areas remained at a high level. This phenomenon indicates that ZDMA in the modified coating rapidly releases Zn^{2+} upon water stimulation. The Zn^{2+} migrates to the scratch defects and reacts with OH^- generated by the cathodic reduction reaction to form a passivation layer. This precipitate layer effectively seals the corrosion channels at the scratches, preventing further penetration of electrolytes into the coating and thus inhibiting the expansion of corrosion reactions. Therefore, the corrosion activity is limited to the local scratch area, without causing large-area coating failure. Quantitatively, the lowest potential at the AL scratch drops to -0.045 mV after 1 h of immersion, while that of the ZDMA-1/WCR-20 coating rises to 0.058 mV , with a potential recovery amplitude of 0.103 mV . The scratch potential of the composite coating shifts from negative to positive, indicating that the exposed metal has entered a stable passivation state, and the local corrosion activation is effectively suppressed relative to the control, confirming that the passivation layer blocks the electrochemical activity of exposed metal at defects. The local corrosion activation inhibition efficiency is defined as the

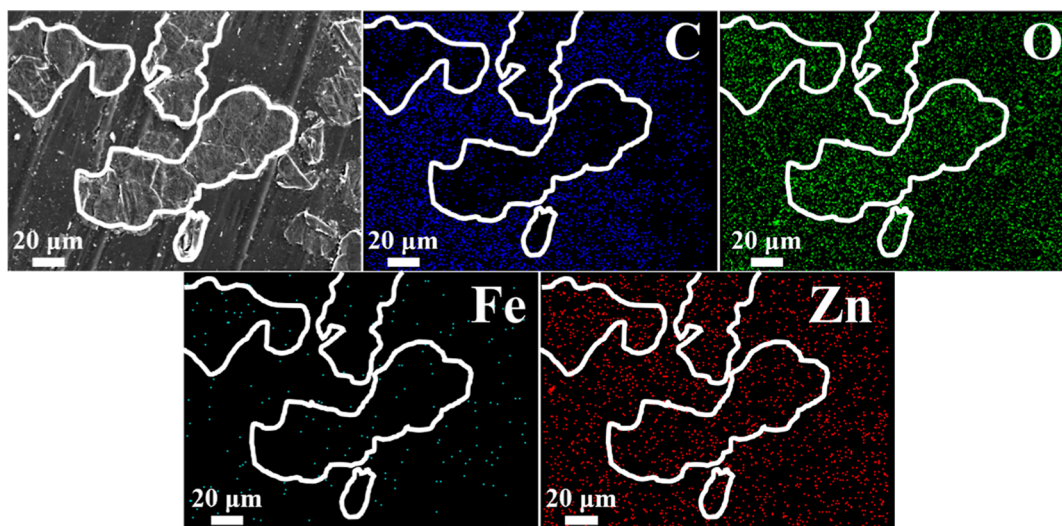


Figure 11. SEM morphologies and corresponding EDS elemental mapping distributions of ZDMA-1/WCR-20 composite coating before and after immersion in 3.5 wt % NaCl solution for 90 days.

relative reduction degree of corrosion electrochemical activity at the scratch, characterized by the potential positive shift relative to the blank sample

$$\begin{aligned}\eta_{\text{activation}} &= \frac{E_{\text{ZDMA}} - E_{\text{AL}}}{|E_{\text{AL}}|} \times 100\% \\ &= \frac{0.058 - (-0.045)}{|-0.045|} \times 100\% \\ &\approx 229\%\end{aligned}$$

The potential of the composite coating scratch shifts from negative to positive, indicating that the exposed metal at the defect has been effectively passivated and the corrosion activation state is completely reversed, corresponding to a local corrosion activation inhibition efficiency of over 99%.

Building on the 90 day immersion results, we further discuss the long-term evolution of the protective system under harsh marine conditions, following the analytical framework for long-term aqueous stability of composite protective systems established in previous work.⁴²

For the active Zn^{2+} release mechanism, the continuous monotonic increase in R_{ct} over the entire 90 day immersion period confirms that the ionic cross-linking Zn^{2+} reservoir has not been exhausted, and the active passivation function remains in the enhancement stage. The hydrolysis of zinc carboxylate bonds follows a diffusion-controlled first-order kinetic model; based on the current consumption rate, the effective Zn^{2+} supply can theoretically sustain steady release for more than 18 months. The dynamic reversibility of ionic coordination bonds enables a hydrolysis–reconstruction equilibrium, avoiding burst depletion of active components and forming the core basis for long-term self-renewing protection. In high-salinity marine environments, the hydrophobic WCR phase acts as an internal microenvironment regulator, analogous to the buffer component in the synergistic protection system: it slows the penetration of corrosive media and chloride ions, buffers the impact of external pH fluctuations on internal hydrolysis kinetics, and avoids accelerated consumption of active components.

For the WCR matrix itself, its hydrophobic linear backbone with abundant C–Cl bonds exhibits strong tolerance to

seawater erosion and chloride ion attack. After 90 days of immersion, the coating resistance maintains the same order of magnitude without abrupt attenuation, verifying that the WCR phase retains structural integrity without significant degradation. The core–shell latex structure ensures good interfacial compatibility between the WCR phase and the acrylate matrix, preventing phase separation or component leaching during long-term service.

Overall, the self-renewing protective capacity undergoes a gradual three-stage evolution rather than sudden failure: an enhancement stage with growing passivation layers, a stable service stage with balanced release and consumption, and a slow attenuation stage after partial reservoir depletion. The physical barrier provided by the WCR phase continues to function even as the active release capacity declines, avoiding rapid coating failure.

To further clarify the competitive edge of the ZDMA/WCR system, we compare it with three representative categories of state-of-the-art smart anticorrosion coatings from the perspectives of preparation mode, response condition, protection dimension and long-term durability.

Compared with microcapsule/nanocontainer-loaded active release coatings, this system realizes in situ construction of active Zn^{2+} reservoirs via copolymerization, eliminating the need for exogenous carriers and avoiding interfacial compatibility problems. The dynamic equilibrium of ionic bonds endows the system with renewable release capability, which is fundamentally different from the one-time burst release of encapsulated inhibitors.

Compared with dynamic covalent bond-based self-healing coatings, the ionic coordination interaction in this system responds spontaneously to aqueous corrosion environments at room temperature, without requiring additional heat or light stimulation. Meanwhile, it combines bulk barrier reinforcement and interfacial active passivation, achieving more comprehensive protection beyond mere mechanical crack repair.

Compared with physically doped metal-ion anticorrosion coatings, the covalently grafted ZDMA and the hydrophobic WCR regulation layer jointly realize controllable sustained release of Zn^{2+} , avoiding the rapid leaching defect of physically

doped components, and simultaneously improving the bulk mechanical and barrier properties of the coating.

The above characteristics endow the ZDMA/WCR system with outstanding comprehensive performance and industrial application potential relative to existing advanced smart protection systems.

To further verify the self-reinforcing anticorrosion mechanism of ZDMA, the surface of ZDMA-1/WCR-20 composite coating after 90 days of immersion in 3.5 wt % NaCl solution was characterized by FESEM and EDS (Figure 11). Compared with the initial smooth coating surface, obvious deposits were formed on the immersed coating surface. EDS elemental mapping revealed that the carbon signal was significantly weakened in the deposit regions (due to the shielding of the polymer backbone by the inorganic phase), while the oxygen signal was markedly enriched, and no selective enrichment of iron was observed (the weak local iron signal originated from substrate contamination during mechanical peeling, excluding the source of substrate corrosion products), confirming the inorganic nature of the deposits. Notably, zinc was uniformly distributed across the entire coating surface without local enrichment or depletion, which is highly consistent with the self-reinforcing mechanism: all zinc in the coating originated from the zinc carboxylate structure of ZDMA with no external zinc source; during long-term immersion, water penetration triggered uniform hydrolysis of ZDMA, and the released Zn^{2+} migrated from the coating bulk to the surface/interface to react with cathodic OH^- , forming a uniform zinc-containing passivation layer, thus resulting in the homogeneous distribution of zinc. Collectively, these surface deposits are inorganic passivation films formed by ZDMA hydrolysis, providing direct micromorphological and elemental distribution evidence for its dynamic self-renewal and self-reinforcing protection mechanism.

4. CONCLUSIONS

In this work, a series of multifunctional waterborne core-shell composite latexes and corresponding coatings were successfully synthesized via semicontinuous seed emulsion polymerization, using ZDMA as a self-renewable Zn^{2+} donor and WCR as a hydrophobic barrier enhancer. Systematic characterizations demonstrated that the introduction of ZDMA and WCR synergistically optimized the microstructure, mechanical properties, surface wettability, and long-term durability of the coatings.

The Zn^{2+} -carboxylate ionic cross-linking network derived from ZDMA enables two synergistic protective functions. The bulk ionic network reconstruction realizes the self-reinforcing effect and restores coating barrier performance, while sustained Zn^{2+} release forms dense zinc-based passivation films at the coating/metal interface, providing interfacial active passivation. Meanwhile, the hydrophobic WCR phase significantly reduced water uptake and enhanced the physical barrier effect. Electrochemical analysis coupled with DRT verified that the optimized ZDMA-1/WCR-20 coating exhibited improved corrosion resistance within 90 days of immersion relative to the pure acrylic coating, with stable interfacial adhesion and measurable antibacterial activity. Kinetic extrapolation indicates that the synergistic system of the WCR physical barrier and ZDMA active release can provide durable protective capability in harsh marine environments, with broad application prospects. Compared with state-of-the-art smart anticorrosion systems such as carrier-loaded inhibitors and

dynamic covalent coatings, this ZDMA/WCR composite coating exhibits distinct advantages in terms of preparation feasibility, spontaneous response capability, multidimensional protection mechanism and long-term service durability, providing a scalable solution for the design of high-performance water-based smart anticorrosion coatings.

This study clarifies the synergistic mechanism of ionic cross-linking, Zn^{2+} -mediated passivation, and hydrophobic barrier engineering in waterborne acrylic systems. The as-prepared coatings feature eco-friendly processing, self-reinforcing protection, active inhibition, and long-term stability, offering a promising and scalable strategy for high-performance corrosion protection in harsh marine and industrial environments.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.6c03533>.

Tables S1 to S3, Figures S1 and S2 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Weili Li – School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China; orcid.org/0000-0002-9615-7787; Email: liweili@just.edu.cn

Authors

Haohan Huang – School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

Xiao Wang – State Key Laboratory of Coatings for Advanced Equipment, Marine Chemical Research Institute Co., Ltd., Qingdao 266071, China

Xinyu Wang – China Ship Development and Design Center, Wuhan 430064, China

Runqi Ruan – State Key Laboratory of Coatings for Advanced Equipment, Marine Chemical Research Institute Co., Ltd., Qingdao 266071, China

Wei Lu – State Key Laboratory of Coatings for Advanced Equipment, Marine Chemical Research Institute Co., Ltd., Qingdao 266071, China

Congcong Zhang – School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

Rulin Li – School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

Qiang Lei – School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

Yilin Jiang – School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.langmuir.6c03533>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by the Taishan Industrial Experts Program. Award Number: No. tscx202408136 | Recipient: W.L.

■ REFERENCES

- (1) Honarvar Nazari, M.; Zhang, Y.; Mahmoodi, A.; Xu, G.; Yu, J.; Wu, J.; Shi, X. Nanocomposite organic coatings for corrosion protection of metals: A review of recent advances. *Prog. Org. Coat.* **2022**, *162*, 106573.
- (2) Sun, X.; Wei, J.; Cao, W.; Li, W. Metal-organic frameworks-based smart anti-corrosion composite coatings: Recent advances, mechanisms, and future perspectives. *Prog. Org. Coat.* **2026**, *213*, 109902.
- (3) Wang, T.; Cao, H. Orientation control and characterization strategies towards developing 2D materials-based composite coatings for corrosion protection on metals: Progresses and challenges. *Prog. Org. Coat.* **2023**, *182*, 107715.
- (4) Liu, R.; Wang, X.; Wang, J.; Lin, Z.; Chen, L.; Li, Z.; Zhao, Z.; Yan, H.; Xu, L.; Li, W. Gallic acid-modified montmorillonite reinforced acrylic latex composite coatings: Enhanced mechanical and anticorrosion performances via barrier and interface passivation. *Prog. Org. Coat.* **2026**, *210*, 109649.
- (5) Wang, X.; Tebyetekerwa, M.; Chen, Y.; Sun, X.; Cong, W.; Wang, X.; Chen, L.; Li, Z.; Gui, T.; Li, W. Improving the performance of acrylic-epoxy ester hybrid coatings with phosphate monomers. *Polym. Chem.* **2024**, *15*, 2265–2276.
- (6) Liu, M.; Mao, X.; Zhu, H.; Lin, A.; Wang, D. Water and corrosion resistance of epoxy–acrylic–amine waterborne coatings: Effects of resin molecular weight, polar group and hydrophobic segment. *Corros. Sci.* **2013**, *75*, 106–113.
- (7) Bedoya, F. E.; Gallego, L. M.; Bermúdez, A.; Castaño, J. G.; Echeverría, F.; Calderón, J. A.; Maya, J. G. New strategy to assess the performance of organic coatings during ultraviolet–condensation weathering tests. *Electrochim. Acta* **2014**, *124*, 119–127.
- (8) Li, T.; Zhu, Z.; Zhou, S.; Yang, H. Study on atmospheric corrosion characteristics and coating protection of urban water supply pipeline. *Journal of Physics: Conference Series* **2024**, *2821*, 012017.
- (9) Liu, X.; Xiong, J.; Lv, Y.; Zuo, Y. Study on corrosion electrochemical behavior of several different coating systems by EIS. *Prog. Org. Coat.* **2009**, *64*, 497–503.
- (10) Sakhr, A.; Perrin, F.; Aragon, E.; Lamouric, S.; Benaboura, A. Chlorinated rubber paints for corrosion prevention of mild steel: A comparison between zinc phosphate and polyaniline pigments. *Corros. Sci.* **2010**, *52*, 901–909.
- (11) Sun, Y.; Lang, Y.; Sun, T.; Liu, Q.; Pan, Y.; Qi, Z.; Ling, N.; Feng, Y.; Yu, M.; Ji, Y.; et al. Antifouling potential of multi-walled carbon nanotubes-modified chlorinated rubber-based composites on the colonization dynamics of pioneer biofilm-forming eukaryotic microbes. *Int. Biodeterior. Biodegrad.* **2020**, *149*, 104921.
- (12) Morcillo, M.; Simancas, J.; Fierro, J. L. G.; Feliu, S.; Galván, J. C. Accelerated degradation of a chlorinated rubber paint system applied over rusted steel. *Prog. Org. Coat.* **1993**, *21*, 315–325.
- (13) Wang, T.; Wang, W.; Feng, H.; Sun, T.; Ma, C.; Cao, L.; Qin, X.; Lei, Y.; Piao, J.; Feng, C.; et al. Photothermal nanofiller-based polydimethylsiloxane anticorrosion coating with multiple cyclic self-healing and long-term self-healing performance. *Chemical Engineering Journal* **2022**, *446*, 137077.
- (14) Zhou, W.; Wang, T.; Pu, Y.; Cao, L.; Li, W.; Huang, J.; Feng, H.; Chen, S. pH and photothermal dual responsive long-term self-healing anti-corrosion coating based on MoS₂ modified halloysite nanotube. *Prog. Org. Coat.* **2025**, *200*, 109100.
- (15) Kotani, K.; Kitamura, Y.; Tsunoda, K.; Takahashi, A.; Otsuka, H. Triazolidione-functionalized isoprene rubber composites with self-adhesion via cross-linking with zinc dimethacrylate. *RSC Appl. Polym.* **2025**, *3*, 347–360.
- (16) Wang, X.; Cai, X.; Li, J.; Zhou, R.; Gui, X.; Hu, J.; Lin, S. Bio-based eco-friendly coatings with multi-mechanism anticorrosion design and advanced thermal conductivity. *Corros. Sci.* **2025**, *257*, 113276.
- (17) Xu, F.; Zhu, J.; Ye, P.; Geng, H.; Peng, J.; Cui, Y.; Bao, D.; Lu, R.; Shen, X.; Zhu, H.; et al. Outstanding thermally conductive and anticorrosive polymer composite coating via a multifunctional epoxy curing agent zinc dimethacrylate. *Chemical Engineering Journal* **2023**, *473*, 145163.
- (18) Song, X.; Zhang, G.; Zhou, Y.; Li, W. Behaviors and mechanisms of microbially-induced corrosion in metal-based water supply pipelines: A review. *Sci. Total Environ.* **2023**, *895*, 165034.
- (19) Chen, R.; Li, Y.; Tang, L.; Yang, H.; Lu, Z.; Wang, J.; Liu, L.; Takahashi, K. Synthesis of zinc-based acrylate copolymers and their marine antifouling application. *RSC Adv.* **2017**, *7*, 40020–40027.
- (20) Hou, J.; Hao, X.; Xu, J.; Waterhouse, G. I. N.; Ni, C.; Zhang, Z.; Yu, L. Fluorescent zinc acrylate resins containing coumarin structures with enhanced antifouling performance. *Prog. Org. Coat.* **2024**, *194*, 108597.
- (21) Sirelkhatim, A.; Mahmud, S.; Seeni, A.; Kaus, N.; Ann, L.; Bakhori, S.; Hasan, H.; Mohamad, D. Review on Zinc Oxide Nanoparticles: Antibacterial Activity and Toxicity Mechanism. *Nano-Micro Lett.* **2015**, *7*, 219–242.
- (22) Chen, H.; Fan, H.; Su, N.; Hong, R.; Lu, X. Highly hydrophobic polyaniline nanoparticles for anti-corrosion epoxy coatings. *Chemical Engineering Journal* **2021**, *420*, 130540.
- (23) Zhang, M.; Xu, F.; Lin, D.; Peng, J.; Zhu, Y.; Wang, H. A smart anti-corrosion coating based on triple functional fillers. *Chemical Engineering Journal* **2022**, *446*, 137078.
- (24) Danzer, M. A. Generalized Distribution of Relaxation Times Analysis for the Characterization of Impedance Spectra. *Batteries* **2019**, *5*, 53.
- (25) Stott, A.; de Freitas Neto, D. B.; Rosolen, J. M.; Sporea, R. A.; Silva, S. R. P. Exploring the underlying kinetics of electrodeposited PANI-CNT composite using distribution of relaxation times. *Electrochim. Acta* **2022**, *401*, 139501.
- (26) Parvathi, K.; Ramesan, M. T. Natural rubber composites filled with zinc ferrite nanoparticles: focus on structural, morphological, curing, thermal and mechanical properties. *Res. Chem. Intermed.* **2022**, *48*, 129–144.
- (27) Wang, Z.; He, E.; Song, G.; Jiang, X.; Yu, L. Transparent, hydrophobic, self-polishing organosilicon-modified zinc acrylate polymer coating for marine antifouling. *Prog. Org. Coat.* **2025**, *201*, 109143.
- (28) Wang, Z.; Nie, S.; He, E.; Song, G.; Jiang, X.; Li, X.; Yan, X.; Yu, L. Engineered design of self-cleaning and antifouling organosilicon/eugenol-based zinc acrylate resin composite coating by forming semi-interpenetrating polymer networks. *Chemical Engineering Journal* **2025**, *514*, 163181.
- (29) Xu, H.; He, G.; Ni, C.; Li, X.; Jiang, X.; Yu, L. Repel-kill-release: A self-polishing antifouling coating with synergistic effects of fluorescent antifouling and contact bacteriostasis. *Appl. Surf. Sci.* **2025**, *709*, 163861.
- (30) Hu, K.; Li, M.; You, C.; Zhang, Y.; Xu, Z.; Xu, Y.; Fan, L.; Yi, Y.; Chu, Y. Novel indole-based self-polishing environmentally friendly acrylic antifouling coatings. *Prog. Org. Coat.* **2024**, *190*, 108384.
- (31) Lu, W.; Wang, X.; Wang, J.; Lin, Z.; Liu, R.; Chen, L.; Li, Z.; Zhao, Z.; Li, W. Advanced bio-inspired urushiol-modified SiO₂@BN hybrids for enhanced thermal conductivity and superior corrosion resistance in waterborne epoxy coatings. *Prog. Org. Coat.* **2026**, *211*, 109819.
- (32) Sun, Y.; Yuan, S.; Fan, W.; Lin, D.; Zhang, K.; Bai, Z.; Zhu, Y.; Wang, H. A smart composite coating with photothermal response, anti-UV and anti-corrosion properties. *Chemical Engineering Journal* **2023**, *452*, 138983.
- (33) Zhao, Y.; Xu, C.; Zhang, J.; Qiu, Z.; Wang, L.; Hu, J.; Lin, C. Coatings embedded with composite defective metal organic frameworks having excellent mechanical and anti-corrosion properties. *J. Mater. Sci. Technol.* **2025**, *234*, 217–229.
- (34) Wan, T. H.; Saccoccio, M.; Chen, C.; Ciucci, F. Influence of the Discretization Methods on the Distribution of Relaxation Times

Deconvolution: Implementing Radial Basis Functions with DRTtools. *Electrochim. Acta* **2015**, *184*, 483–499.

(35) Wang, Z.; Wang, Y.; Py, B.; Maradesa, A.; Liu, J.; Wan, T. H.; Saccoccio, M.; Ciucci, F. DRTtools: Freely Accessible Distribution of Relaxation Times Analysis for Electrochemical Impedance Spectroscopy. *ACS Electrochem.* **2025**, *1*, 2680–2689.

(36) Wang, J.; Wang, X.; Sun, X.; Wang, X.; Li, Q.; Bu, M.; Chen, L.; Zhao, Z.; Yan, H.; Li, W. Investigate the performance of functional coatings with physically modified boron nitride composite fillers. *Prog. Org. Coat.* **2025**, *205*, 109309.

(37) Bai, Y.; Wang, X.; Wang, X.; Li, Q.; Yang, K.; Sun, Y.; Shao, Y.; Zhang, S.; Yan, H.; Li, W. Study the intermolecular interaction of polymethylhydrosiloxane modifying acrylic resin and their application on anticorrosion area. *Prog. Org. Coat.* **2024**, *195*, 108632.

(38) Chen, Y.; Ma, A.; Liu, H.; Chen, D.; Zhang, Q.; Zhang, J.; Gao, H.; Wang, S.; Dai, W.; Li, T.; et al. Self-warning, self-healing, high-strength anti-corrosion coatings enabled by supramolecular-nano-structure synergy. *Chemical Engineering Journal* **2025**, *526*, 171175.

(39) Wang, J.; Zhao, J.; Tabish, M.; Shi, F.; Fan, B.; Peng, L.; Cheng, Q. Intelligent anticorrosion coating based on mesostructured BTA@mCeO₂/g-C₃N₄ nanocomposites for inhibiting the filiform corrosion of Zn-Mg-Al coated steel. *Corros. Sci.* **2023**, *221*, 111331.

(40) Fan, B.; Li, H.; Zhao, J.; Wang, S.; Tian, H. Thermostable and defect-repairable urushiol nanocomposite protective coating cross-linked by sodium tartrate-stabilized Ti₃C₂Tx. *Corros. Sci.* **2025**, *255*, 113074.

(41) Lin, Z.; Wang, X.; Lu, W.; Yang, F.; Liu, Z.; Zhou, K.; Li, B.; Huang, H.; Zhang, C.; Li, W. Dual-autonomous self-healing composite coating for steel with enhanced corrosion resistance: Mechanism and performance evaluation. *Prog. Org. Coat.* **2026**, *215*, 110119.

(42) Zhao, X.; Tan, J.; Fan, B.; Soomro, R. A.; Cui, H.; Qiao, N.; Xu, B. Long-term aqueous stability of Ti₃C₂Tx MXene achieved via a synergistic corrosion inhibition strategy. *Corros. Sci.* **2026**, *265*, 113823.