

Dual-autonomous self-healing composite coating for steel with enhanced corrosion resistance: Mechanism and performance evaluation

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ABSTRACT

Thermodynamic incompatibility between mobile healing agents and rigid polymer matrices remains a critical bottleneck for dual-mechanism self-healing anticorrosive coatings. To address this issue, we developed a molecular compatibilization strategy using urea-functionalized polysiloxane silica sol (Urea-SI) grafted onto an acrylic resin backbone. This design achieves homogeneous nanodispersion of methyl silicone oil (MSO) as sub-100 nm healing reservoirs, while constructing a stimulus-free reversible hydrogen-bonding network via urea moieties to enable intrinsic self-healing. The optimal formulation (5 wt% Urea-SI) balances mechanical robustness and self-healing efficiency, maintaining $|Z|_{0.01\text{Hz}} > 7 \times 10^9 \Omega \cdot \text{cm}^2$ after 27 days of immersion in 3.5 wt% NaCl solution, with a corrosion current density two orders of magnitude lower than control systems and repeatable self-healing (≥ 5 cycles). Compared with traditional microcapsule-based and dynamic covalent network coatings, this strategy exhibits superior scalability, long-term stability, and avoids the inherent trade-off between mechanical strength and healing performance. This work provides a generalizable molecular engineering principle for high-performance autonomous protective coatings, with promising applications in harsh marine and industrial environments.

1. Introduction

Self-healing coatings represent a transformative advancement in corrosion protection technology, offering the potential to autonomously mitigate damage from scratches, cracks, or environmental degradation without external intervention. Their significance is particularly pronounced in demanding applications such as offshore platforms, ship hulls, and aerospace structures, where maintenance access is limited and failure consequences are severe. Over the past two decades, extensive research has focused on developing intelligent coating systems capable of restoring barrier functionality through either extrinsic mechanisms—such as the release of encapsulated healing agents—or intrinsic mechanisms—relying on reversible dynamic bonds within the polymer network [1]. While both strategies have demonstrated proof-of-concept success, a persistent and fundamental challenge remains unresolved: the intrinsic incompatibility between mobile, low-surface-energy healing

phases (e.g., polydimethylsiloxane oils) and rigid, high-crosslink-density organic matrices (e.g., acrylic or epoxy resins) inevitably leads to macroscopic phase separation during film formation [2], thereby compromising both mechanical integrity and long-term corrosion resistance [3].

This incompatibility stems from the large disparity in solubility parameters and intermolecular interactions between non-polar silicone-based fluids and polar polymer backbones. When incorporated at concentrations sufficient to enable effective healing ($>3\text{--}5$ wt%), methyl silicone oil (MSO) tends to aggregate into micron-scale domains, creating percolation pathways that facilitate rapid electrolyte penetration. Electrochemical impedance spectroscopy (EIS) studies by Wang et al. [4] and Cao et al. [5] have consistently shown that such phase-separated morphologies manifest as Warburg diffusion tails (Z_w) in Nyquist plots after only 7–14 days of immersion, signaling active corrosion beneath the coating. Moreover, these dispersed MSO-rich

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regions act as stress concentrators, significantly reducing tensile strength, pencil hardness, and impact resistance—properties critical for coatings subjected to mechanical wear or thermal cycling. Consequently, conventional blending approaches fail to achieve the dual objectives of high mechanical robustness and efficient autonomous healing.

To circumvent this limitation, researchers have predominantly turned to microencapsulation technologies. Pioneering work by White et al. [6] introduced dicyclopentadiene-filled urea-formaldehyde microcapsules into epoxy matrices, enabling one-time autonomic repair. Subsequent studies reported the construction of intrinsic/extrinsic self-healing anticorrosion coatings, in which the intrinsic self-healing was realized by dynamic covalent/noncovalent interactions, and the extrinsic self-healing relied on the release of healing agents to repair coating defects, providing a feasible strategy for the design of physical barrier-repaired self-healing coatings [7]. Despite these innovations, microencapsulation strategies suffer from three critical drawbacks. First, the fabrication process—often involving interfacial polymerization, coacervation, or layer-by-layer assembly—is complex, costly, and difficult to scale industrially [7–9]. Second, the capsules themselves introduce heterogeneities that weaken the coating matrix and reduce adhesion to metallic substrates [10]. Third, and most fundamentally, the healing capacity is finite and non-renewable; once the capsule ruptures, no further repair is possible at that site [10]. These limitations render microcapsule-based systems unsuitable for long-term, multi-damage scenarios typical in marine environments.

In parallel, intrinsic self-healing systems based on dynamic covalent or supramolecular chemistry have gained traction. Reversible reactions such as Diels-Alder cycloadditions [6], disulfide exchange [11], and imine bond rearrangement [12] enable repeatable healing, while hydrogen-bonding networks offer stimulus-free repair at ambient conditions. However, these systems face their own trade-offs. Dynamic covalent networks often require elevated temperatures ($>60\text{ }^{\circ}\text{C}$) or UV irradiation to activate bond exchange, precluding true autonomy in field applications [13]. Supramolecular systems, though autonomous, typically exhibit low glass transition temperatures (T_g) and reduced cross-link density to maintain chain mobility, resulting in poor hardness, creep resistance, and barrier performance [1]. As recently emphasized by Schlemper and Pezzin [14], “the quest for room-temperature, multi-cycle, and mechanically robust self-healing remains the ‘holy grail’ of coating design.”

Recent efforts to combine extrinsic and intrinsic mechanisms—so-called dual-autonomous systems—have shown promise but still grapple with the core compatibility issue. For instance, Wang et al. [15] integrated MSO with a polydimethylsiloxane elastomer containing imine bonds, achieving transparent self-healing films; however, the system lacked the rigidity required for structural corrosion protection. Similarly, blends of acrylic resins with PDMS derivatives via sol-gel processes [16] often result in coarse phase morphologies unless compatibilizers or coupling agents are added—a solution that introduces additional chemical complexity without guaranteeing nanoscale homogeneity.

While numerous dual-mechanism self-healing anticorrosive coatings (e.g., microcapsule-based systems, dynamic covalent network coatings) have been reported, most suffer from inherent limitations: microcapsule-based coatings sacrifice mechanical robustness due to structural defects and only enable single-cycle healing, while dynamic covalent network coatings face a severe trade-off between mechanical strength and self-healing efficiency, often requiring external stimuli and exhibiting poor long-term stability under corrosive conditions. Moreover, the thermodynamic incompatibility between mobile healing agents and rigid polymer matrices—a core bottleneck limiting the performance of such coatings—has not been effectively addressed by traditional compatibilization approaches. In contrast, this work differs from previous studies by proposing a multifunctional molecular compatibilization strategy using urea-functionalized polysiloxane silica sol (Urea-SI), which integrates three key functions into a single mediator:

supramolecular hydrogen-bonding motifs for intrinsic self-healing, polysiloxane segments for regulating interfacial compatibility, and urea moieties for enhancing matrix adhesion. This design not only resolves the longstanding phase separation issue between methyl silicone oil (MSO) and acrylic resin but also breaks the traditional trade-off between mechanical robustness and self-healing efficiency. Unlike conventional strategies that focus solely on either healing agent delivery or dynamic network construction, our molecular engineering approach achieves a synergistic balance of mechanical performance, repeatable self-healing, and long-term corrosion resistance, while maintaining industrial scalability—these features collectively distinguish our work from previous research and provide a new generalizable principle for the design of high-performance self-healing anticorrosive coatings.

2. Experimental section

2.1. Materials

3-Isocyanate-propyl trimethoxysilane (C.P.) was supplied by Zhongshan Gragon Chemical Trading Co., Ltd., LTD. bis(3-aminopropyl)-terminated polydimethylsiloxane (C.P.) was supplied by Guangzhou Xinguang Chemical Technology Co., Ltd., China. Methyl trimethoxysilane (MTMS, C.P.) was supplied by Shandong Shuntai New Materials Co., Ltd., China. Methyl silicone oil (MSO, C.P.) with a viscosity of 100 cSt, γ -aminopropyl triethoxysilane (KH-550, C.P.), and γ -methyl acryloxypropyl trimethoxysilane (KH570, C.P.) were supplied by Dongguan Kangjin New Materials Co., Ltd., China. Ethanol (C.P.), butyl acetate (C.P.) were provided by Jiangsu Wuxi Jiaseng Pharmaceutical Chemical Co., Ltd. Styrene (St, C.P.), methyl methacrylate (MMA, C.P.), isooctyl acrylate (2-EHA, C.P.), and hydroxyethyl acrylate (HEA, C.P.) were provided by Chinasun Specialty Products Co., Ltd., Benzoyl Peroxide (BPO, AR) was obtained by Shanghai Macklin Biochemical Co., Ltd., China.

2.2. Synthesis process

Initially, a modified silica sol containing urea-terminated polysiloxane (denoted as Urea-SI) was synthesized (as is presented in Fig. 1). Subsequently, Urea-SI modified acrylic resin (named as AUrea-SI) was synthesized via solution polymerization (as is presented in Fig. 2). The polymerization mixture comprised MMA and St as hard monomers, 2-EHA as the soft monomer, and HEA as the functional monomer. Benzoyl peroxide (BPO) was first dissolved in this monomer mixture and added synchronously with the monomers to initiate the polymerization reaction. The synthesized Urea-SI was combined with the acrylic resin in the reaction progress. During this composite formation, reactions occurred between the active groups on the Urea-SI surface (e.g., silanol groups, vinyl groups) and complementary groups within the acrylic resin, resulting in chemical bonding between the two phases. Finally, methyl silicone oil (MSO, 1 wt% based on the total resin mass) was added to this mixture at room temperature to impart self-healing properties for the composites. The specific formulas is summarized in Table S1, and the detailed preparation process is provided in the supplementary document.

To evaluate the effect of Urea-SI loading, composites with varying Urea-SI content relative to the total composite resin mass were prepared: 1, 3, 5, 7, and 9 wt%. These composites are designated MSO/AUrea-SI-X, where X represents the mass percentage of Urea-SI in the solid resin phase. Fig.S1 compares the integration behavior of representative composite MSO/AUrea-SI-5 vs. control blend (methyl silicone oil/MSO + conventional acrylic resin). For the control system, MSO/conventional acrylic resin, undergoes significant macrophase separation, resulting in a heterogeneous morphology with clearly discernible boundaries between the immiscible phases. In stark contrast, the MSO/AUrea-SI-5 composite exhibits a uniform, homogeneous, and semi-transparent appearance. This observed morphological homogeneity

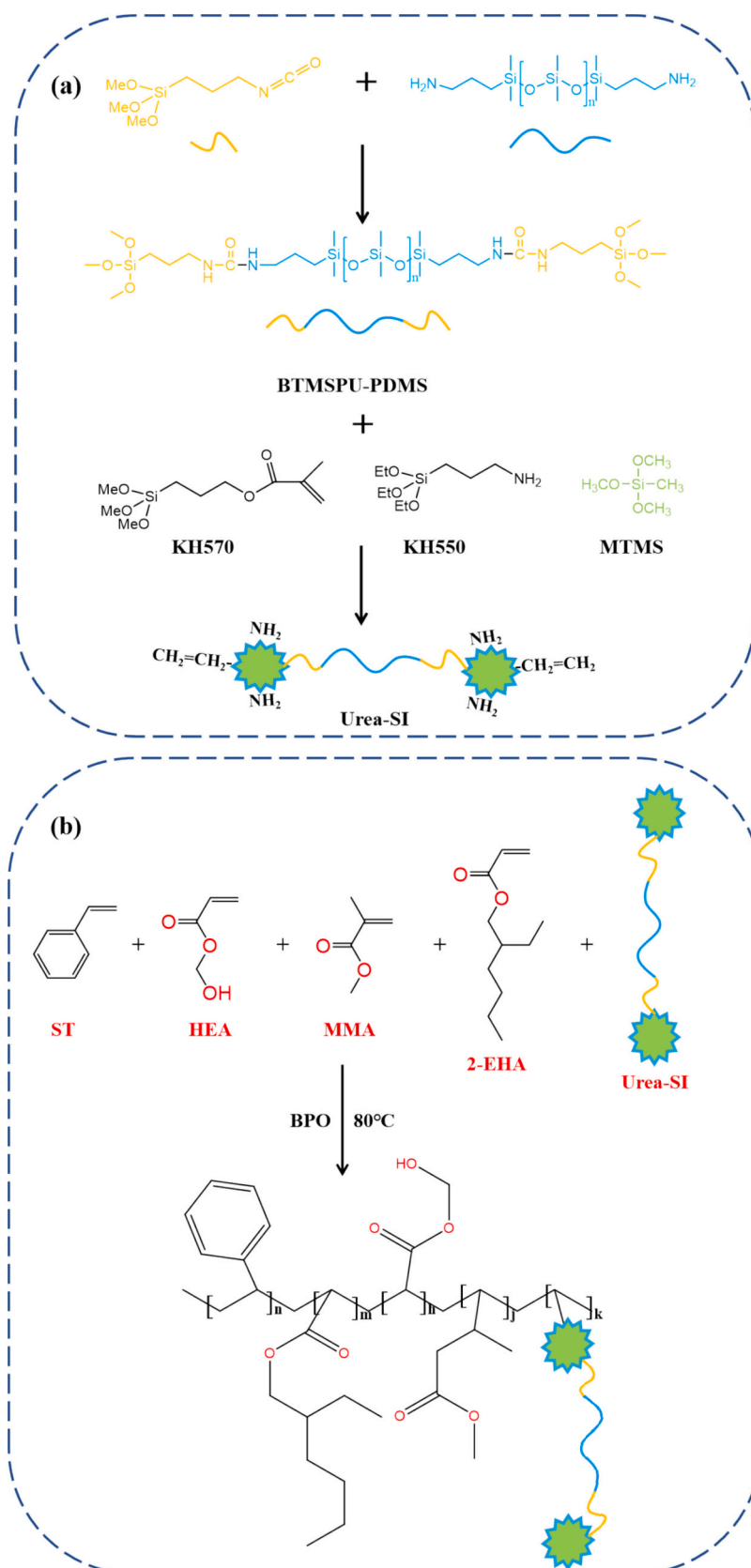


Fig. 1. Synthesis Scheme of Urea-SI(a) and AUrea-SI(b).

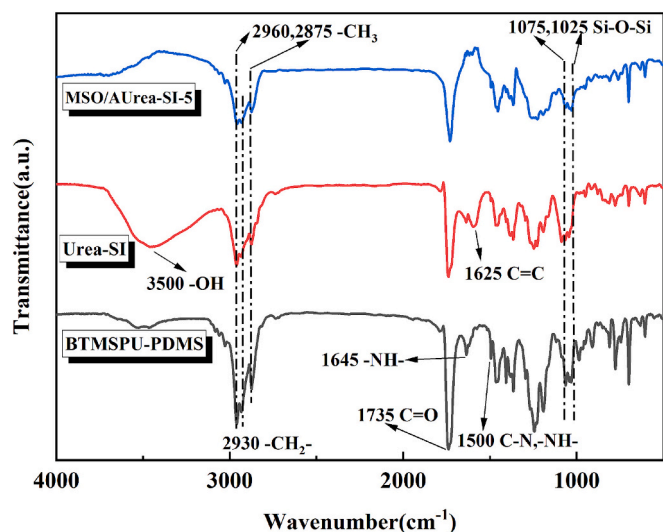


Fig. 2. FTIR spectra of BTMSPD-PDMS, Urea-SI, and the resultant MSO/AUrea-SI-X (MSO/AUrea-SI-5 was taken as example).

suggests the absence of large-scale phase separation and provides strong visual evidence for the successful molecular-level integration of MSO. The silicone oil is effectively sequestered and stabilized within the specifically designed segregated domains of the Urea-SI, which is a key finding of this study. This enhanced compatibility is crucial for improving the material's performance in applications such as anti-corrosion area.

To investigate the cross-sectional morphology of MSO/AUrea-SI-X-derived coatings and establish the correlation between their morphological features and the performance of cured films, Q235 carbon steel panels and silica glass slides were employed as substrates. The chemical composition (wt%) of the Q235 steel is as follows: C (0.14–0.22), Mn (0.30–0.65), Si (≤ 0.30), S (≤ 0.050), P (≤ 0.045), and Fe (balance). Prior to coating deposition, the steel panels were sequentially polished with 400–2000 grit silicon carbide sandpaper to achieve a uniform surface roughness, followed by ultrasonic cleaning in ethanol for 15 min to eliminate surface contaminants (e.g., dust particles and oil residues). The coatings were dried at 80 °C for 2 h, followed by storage at room temperature for an additional 7 days. Coating thickness was controlled at 90 μm for steel panels and 60 μm for silica glasses.

2.3. Material characterization

Fourier transform infrared (FTIR) spectra of the samples were recorded using a Nicolet iS50 Fourier transform infrared spectrometer (Thermo Fisher Scientific, USA) to analyze the chemical structure and functional group interactions. Thermal properties of the samples were evaluated via two complementary techniques: Differential Scanning Calorimetry (DSC) and Thermogravimetric-Differential Thermal Analysis (TG-DTA). DSC tests were performed using a Diamond DSC 8000 apparatus, with heating and cooling cycles conducted between -50 °C and 100 °C at a rate of 10 °C $\cdot\text{min}^{-1}$ under a nitrogen flow of 50 mL $\cdot\text{min}^{-1}$. The thermal stability of the coatings was analyzed using a Diamond TG-DTA thermogravimetric analyzer (Perkin Elmer Instruments). The mechanical properties of the coatings were tested using various instruments in accordance with relevant national standards (GB/T). Specifically, the toughness was evaluated with a QTY-32 type paint film bending tester (GB/T 1731–2020), the impact resistance was measured using a BGD 302 tubular paint film impactor (GB/T 20624.2–2006), and the hardness was assessed via the pencil hardness method (GB/T 6739–2006). Contact angle measurements were carried out using a Theta Lite Contact Angle Meter (Biolin Scientific) with distilled water, where the surface tension parameters of water were set

as follows: total surface free energy $\gamma = 72.8$ mN/m, dispersion component $\gamma_d = 21.8$ mN/m, and polar component $\gamma_p = 51$ mN/m. The surface and cross-sectional morphologies of the cured MSO/AUrea-SI-X composite coatings were characterized using a Field Emission Scanning Electron Microscope (FESEM, SEM4000, CIQTEK Co., Ltd) and a Confocal Laser Scanning Microscope (optical profilometer, OLS4000, Olympus Corporation, Japan). Micro-area electrochemical testing was performed using a VersaSCAN micro-area electrochemical microscope (Advanced Measurement Technology Inc.). The corrosion resistance of the coated samples was investigated using a CHI660A electrochemical workstation by analyzing Tafel polarization curves and AC impedance (EIS). For these electrochemical tests, the cured coatings were immersed in a 3.5 wt% NaCl solution, with the coated steel plate as the working electrode (test area: 9.6 cm 2), a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Detailed test parameters were set as follows: Tafel polarization curves were scanned at a rate of 1 mV $\cdot\text{s}^{-1}$ within a potential range of ± 250 mV relative to the open circuit potential (OCP), with samples immersed for 30 min to stabilize the OCP before testing; EIS tests were conducted over a frequency range of 10^5 Hz to 10^{-2} Hz with an AC amplitude of 10 mV (sinusoidal voltage), and the same 30 min pre-test immersion time was adopted (long-term immersion tests up to 27 days were also performed as described in the manuscript). Additionally, Scanning Kelvin Probe (SKP) tests were conducted using a platinum–iridium (Pt–Ir) probe (tip diameter: ~ 50 μm) in non-contact mode, with a scanning area of 5 mm $\times$ 5 mm, step size of 50 μm , and ambient conditions maintained at room temperature (25 ± 1 °C) and relative humidity (RH) of $45 \pm 5\%$; the probe was calibrated with a copper reference electrode before each test to ensure potential accuracy.

3. Results and discussion

3.1. Structure and properties analysis of the composite resin

First, the validity of the synthetic process was confirmed by comparing the FTIR of intermediate products at different stages. Fig. 2 compares the changes in the FTIR spectra of the synthesized BTMSPD-PDMS, Urea-SI, and MSO/AUrea-SI composite (MSO/AUrea-SI-5 was used as an example). For the BTMSPD-PDMS intermediate, no doublet corresponding to the asymmetric and symmetric stretching vibrations of free $-\text{NH}_2$ groups (characteristic of amino-terminated PDMS) was detected in the 3300 – 3400 cm $^{-1}$ range [17]. Instead, a broad peak appeared at 3500 cm $^{-1}$, assigned to the N–H stretching vibration of urea linkages, confirming that amino groups reacted with an equimolar amount of isocyanate to form secondary amine-based urea bonds. Peak broadening arises from hydrogen-bonding interactions. Concurrently, a weak peak at 1645 cm $^{-1}$ is attributed to the scissoring bending vibration of secondary amine hydrogen, while a strong absorption at 1735 cm $^{-1}$ corresponds to the C=O stretching vibration of the urea carbonyl group [18]. A medium-intensity peak at 1500 cm $^{-1}$ originates from the coupling of N–H bending and C–N stretching vibrations. Collectively, these results verify that amino groups in amino-terminated silicone oil reacted covalently with the isocyanate groups of 3-isocyanatopropyltrimethoxysilane, forming urea linkages.

In addition, Urea-SI reveals a new peak at 1625 cm $^{-1}$, assigned to C=C stretching vibrations. This peak was introduced by KH570 during the sol-gel reaction, enabling Urea-SI to covalently link with acrylic resin monomers via solution polymerization. Furthermore, for the MSO/AUrea-SI-5 composite, the disappearance of the 1625 cm $^{-1}$ C=C peak confirmed complete consumption of double bonds during copolymerization [16]. Meanwhile, the blended MSO enhances the intensity of the 1258 cm $^{-1}$ peak, which corresponds to the scissoring bending vibration of CH_3 groups in silicone chains. These spectral changes preliminarily validate the effectiveness of the synthetic reactions.

Then, TGA and DSC were conducted to investigate the influence of the MSO/AUrea-SI interplay on the thermodynamic behavior of the

cured coating. As is presented in Fig. 3(a), during the TGA test, upon increasing the testing temperature, all samples exhibited an initial gradual mass loss ($\leq 5\%$), which is attributed to the volatilization of residual organic components (e.g., solvents, unreacted monomers). Notably, when the temperature reached the range of 350–380 °C, a significant mass loss commenced, which is characterized by a distinct thermal decomposition plateau. This indicates the onset of primary thermal degradation within this temperature region. Crucially, the TGA data reveal that thermal stability increases progressively with higher Urea-SI content. Specifically, at any given temperature within the decomposition onset region, coatings richer in Urea-SI display enhanced resistance to mass loss. Furthermore, the residual char yield at elevated temperatures (e.g., 600 °C) also rises with increasing Urea-SI concentration [19]. This enhanced thermal stability is primarily ascribed to two factors: (i) The superior bond strength of the Si—O covalent bonds ($\approx 450 \text{ kJ mol}^{-1}$) within Urea-SI, which is significantly higher than that of the C—C ($\approx 332 \text{ kJ mol}^{-1}$) and C—O ($\approx 326 \text{ kJ mol}^{-1}$) bonds predominant in the Hydroxy-functional Acrylic Resin (HAR) component. Consequently, cleavage of the Si—O network demands substantially higher energy input [18]. (ii) The abundant hydroxyl (—OH) groups present on the surface of the silica sol particles generated via the sol-gel reaction in Urea-SI. These groups facilitate the formation of strong intermolecular hydrogen bonds within the composite matrix. This extensive hydrogen bonding network effectively mitigates the detrimental impact of elevated temperatures on coating stability [20,21].

As shown in Fig. 3(b), the DSC curves of the cured MSO/Aurea-SI-X composites exhibit a single, broad glass transition region within the tested temperature range of -50 to 100 °C. The acrylate component in AUrea-SI-X has a predefined T_g of ≈ -10 °C (estimated by the FOX equation). Notably, the T_g of the test samples shifts to higher values with increasing Urea-SI content [17]. This behavior demonstrates that chemical bonding between HAR and Urea-SI components effectively suppresses phase separation and mitigates polarity-induced incompatibility [22]. Furthermore, strong hydrogen bonding and polar group interactions within the silica sol of Urea-SI significantly restrict segmental mobility in the acrylate polymer chains, thus causing a significant increase in the T_g of the composite coating. In addition, the physical MSO component (incorporated at 1 wt%) typically exhibits a glass transition between -120 and -125 °C, which was not detected within this study's temperature range. Nonetheless, it can be inferred from the molecular structure of MSO that this low content enhances the toughness of the cured coating through the flexibility of its molecular

chains.

DSC analysis reveals that the rigid Urea-SI and the flexible MSO exert distinct influences on the cured coating. The analysis of mechanical properties—including pencil hardness, impact resistance, and flexibility—across coatings (Table 1) with varying mass ratios demonstrates a consistent trend: pencil hardness progressively increases with elevated Urea-SI content, which is attributed to the enhanced cross-linking density of the urea modified silica network. Conversely, impact resistance and flexibility remain well-preserved owing to the effective integration of low T_g MSO, which acts as a toughening agent. The resultant composite coating exhibits performance metrics aligned with practical application requirements.

The silicone components within the composite coating significantly influenced its surface characteristics. As shown in Fig. 4(a), the coating exhibited hydrophobicity, with its water contact angle rising significantly from 95° to 108° as the Urea-SI content increased. The coating's surface free energy, calculated from diiodomethane probe measurements and presented in Table 2, demonstrated a concurrent significant decrease in total surface free energy with increasing Urea-SI content. Correspondingly, Fig. 4(b) shows that the water absorption rate of the coatings declines progressively with elevated Urea-SI loading, falling from an initial 2.38% to a minimum of 1.89% after 60 h of immersion in water.

The observed phenomenon primarily stems from the nonpolar organic groups (e.g., $-\text{CH}_3$) bonded to silicon atoms, which shield the highly polar Si—O backbone, significantly reducing surface polarity. The hydrophobicity and low polarity of these side groups collectively

Table 1

Mechanical properties of MSO/Aurea-SI-X composite coatings.

	Pencil hardness	Impact resistance (kg·cm)	Toughness (mm)
MSO/AUrea-SI-1	HB	50	0.5
MSO/AUrea-SI-3	H	50	0.5
MSO/AUrea-SI-5	H	50	0.5
MSO/AUrea-SI-7	2H	50	0.5
MSO/AUrea-SI-9	2H	50	0.5
HAR	2B	50	0.5

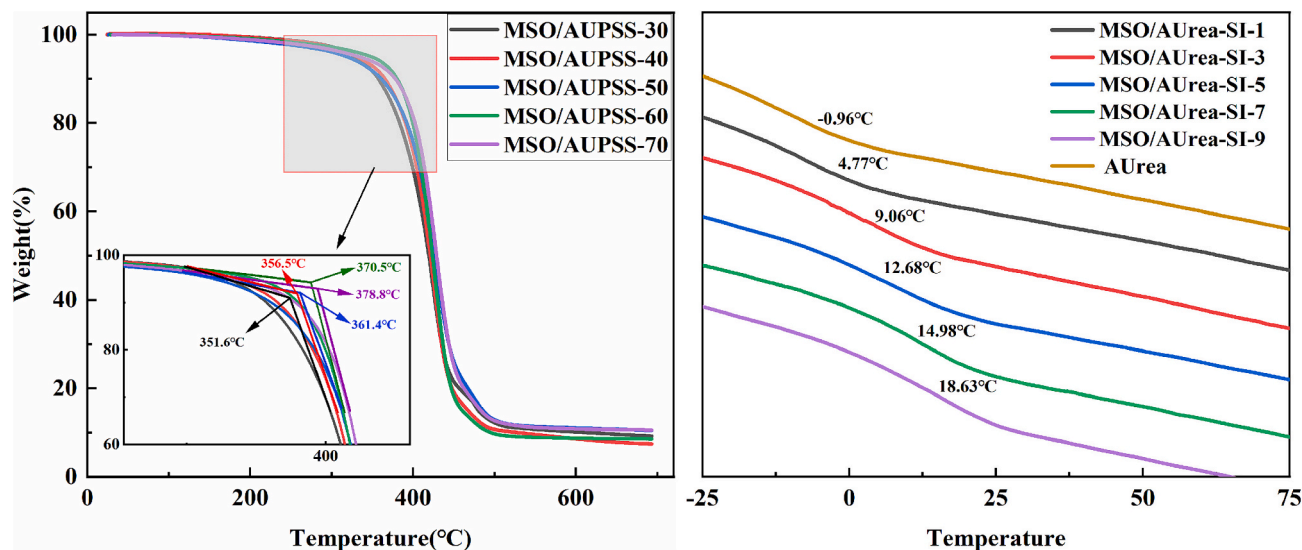


Fig. 3. (a) TGA curve and (b) DSC curve of MSO/Aurea-SI-X composite (X = 1–9), varied with the relative content of Hydroxy-functional Acrylic Resin (HAR) and Urea-SI; MSO = 1 wt%.

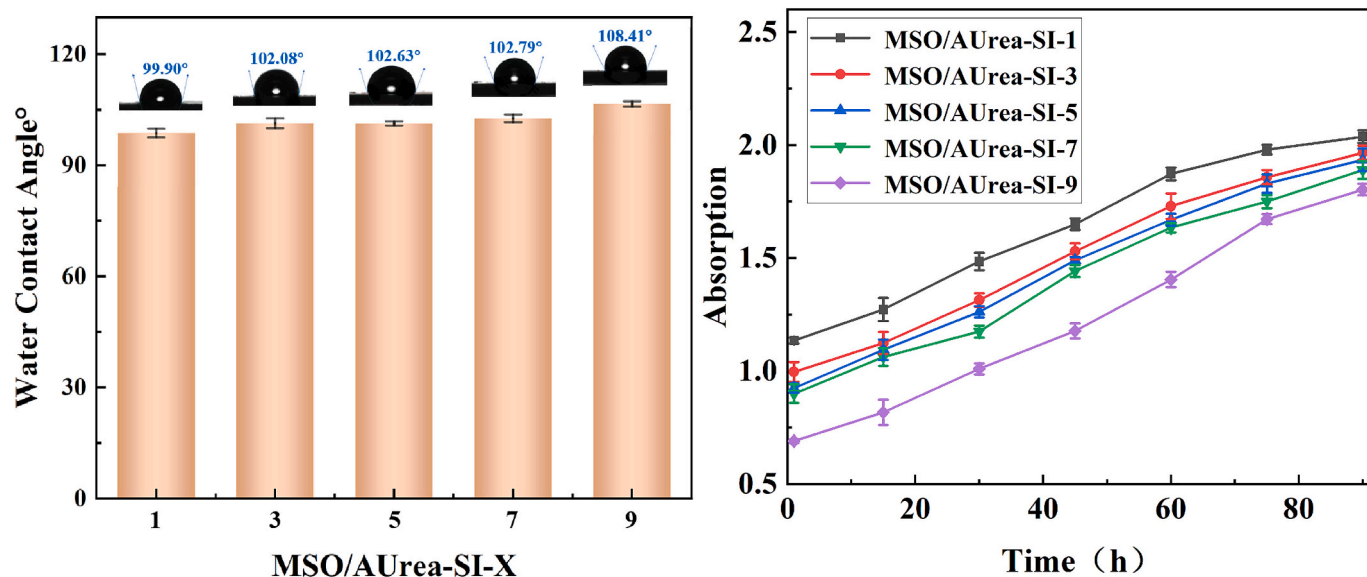


Fig. 4. Variation trend of surface contact angle with different component ratio in MSO/AUrea-SI-X composite coatings.

Table 2

The surface tension properties of the MSO/AUrea-SI-X composite coatings.

Sample	Dispersive component (γ_s^d)	Polar component (γ_s^p)	Surface free energy (γ_s)
MSO/AUrea-SI-1	32.39 ± 0.18 mN/m	0.38 ± 0.05 mN/m	32.77 ± 0.23 mN/m
MSO/AUrea-SI-3	29.92 ± 0.15 mN/m	0.27 ± 0.04 mN/m	30.19 ± 0.19 mN/m
MSO/AUrea-SI-5	27.60 ± 0.09 mN/m	0.45 ± 0.01 mN/m	28.05 ± 0.10 mN/m
MSO/AUrea-SI-7	29.31 ± 0.11 mN/m	0.18 ± 0.04 mN/m	29.49 ± 0.15 mN/m
MSO/AUrea-SI-9	24.31 ± 0.10 mN/m	0.13 ± 0.03 mN/m	24.44 ± 0.13 mN/m

contribute to the hydrophobic nature of the entire coating. Furthermore, the large bond angle ($\approx 143^\circ$) and bond length (≈ 1.64 Å) of the Si—O bonds induce a helical conformation in the molecular chains, imparting high flexibility and facilitating segmental motion. The C—H bonds in the organosilicon side chains exhibit minimal polarity, resulting in weak intermolecular van der Waals forces—substantially weaker than the dipole interactions in fluorinated materials. Consequently, the low cohesive energy density (≈ 200 MJ/m³) enables facile surface migration of molecules, forming a low-energy surface. The nonpolar methyl groups dynamically migrate to the coating–air interface, creating a molecularly smooth, low-energy boundary. This continuous migration mechanism sustains low surface energy, effectively inhibiting the adsorption of polar substances (e.g., water, ice, contaminants) [23–25].

3.2. Morphology and self-healing behavior of MSO/AUrea-SI composite coatings

To investigate the interfacial interactions between different components in the MSO/AUrea-SI composite coating, MSO/AUrea-SI-5 was selected as a representative sample. The surface and cross-sectional morphologies of the cured coating were characterized.

As illustrated in Fig. 5a, the cured coating exhibits a smooth surface with uniformly dispersed components. This morphological feature is

attributed to the formation of chemical bonds and strong hydrogen bonding interactions between MSO and Urea-SI segments, which effectively suppress the phase separation tendency of the two components. Such a smooth and homogeneously distributed surface endows the coating with excellent mechanical barrier protection and enhanced corrosion resistance. As shown in Fig. 5b, the cross-sectional morphology of the coating reveals that the blended low-molecular-weight MSO exhibits incompatibility with the AUrea-SI matrix; instead, it is encapsulated within the cured coating, forming discrete silicone oil pools with an approximate diameter range of 5–50 nm. As previously discussed, due to the flexible polymer chain structure of silicone and its low cohesive energy density, the embedded LMW MSO is spontaneously released upon coating damage. The subsequent flow of silicone oil at the damage site forms a continuous protective film, thereby realizing the self-healing functionality of the coating [26–29].

Notably, all MSO/AUrea-SI-X formulations (X = 1, 3, 5, 7, 9) share a structurally consistent morphological framework, attributed to the universal compatibilization effect of Urea-SI and identical synthetic/curing conditions. The surface of each coating is smooth and free of macroscopic phase separation, while the cross-section features MSO dispersed as discrete nanoscale reservoirs (<100 nm) within the acrylic matrix. The only morphological difference among formulations is the quantitative variation in the number of MSO nanoreservoirs: increasing Urea-SI content from 1 to 5 wt% enhances compatibilization, leading to a gradual increase in the number of uniformly dispersed MSO nanoreservoirs; beyond 5 wt% Urea-SI, slight aggregation of Urea-SI domains occurs, but the core structure of MSO nanoreservoirs is retained. This quantitative difference is sufficiently reflected in the performance trends (e.g., corrosion resistance, hydrophobicity) of the formulations, and the FESEM images of MSO/AUrea-SI-5—representing the optimal structural state—fully capture the key morphological features of the designed system, thus no additional FESEM images are required. Fig. 5(c) and (d) display the surface and cross-sectional morphologies of the pure AUrea-SI coating, whose homogeneous composition endows it with a uniform and flat surface as well as interior, which is distinctly different from the samples prepared in this study.

To elucidate the self-healing mechanism driven by interfacial compatibility, a controlled experiment was performed on MSO/AUrea-SI-5. Multiple parallel scratches (depth: 20.3 ± 1.2 μm) were created using a diamond indenter (500 g load) under identical controlled conditions (25 °C, 60% RH). Laser confocal microscopy verified that the initial morphology (width, depth, edge sharpness) of these scratches was

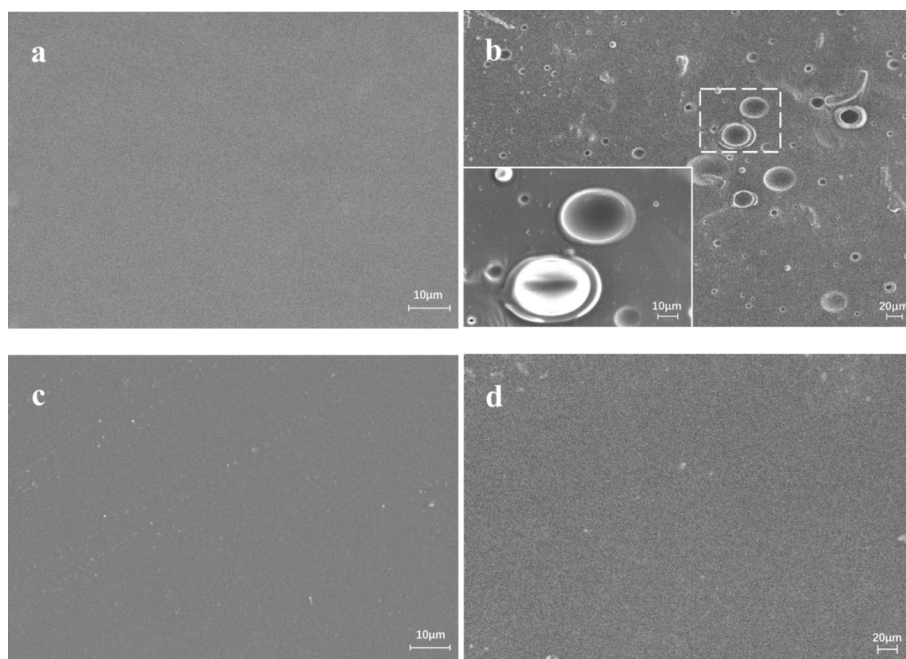


Fig. 5. FESEM images of MSO/Aurea-SI-5 composite coating and pure AUrea-SI coating: (a) Surface morphology of MSO/Aurea-SI-5; (b) Cross-sectional morphology of MSO/Aurea-SI-5; (c) Surface morphology of pure AUrea-SI; (d) Cross-sectional morphology of pure AUrea-SI. MSO/Aurea-SI-5 (5 wt% Urea-SI) is selected as the representative sample due to its optimal structural balance and comprehensive performance, whose morphological features sufficiently illustrate the core design principle of the study.

highly consistent, eliminating interference from inherent differences between samples. FESEM images were captured for representative scratches: one immediately after scratching (unrepaired state) and another after 24 h of self-healing. As shown in Fig. 6, the self-healed scratch exhibited $\sim 85\%$ depth reduction with blurred edges and homogeneous exudate filling, while the unrepaired scratch retained sharp edges and no filling. This observation is consistent with the self-healing efficiency quantified by laser confocal microscopy on the same scratch ($\sim 85\%$ depth reduction after 48 h), confirming the morphological changes induced by self-healing. The results demonstrate a synergistic mechanism: (1) Reformed hydrogen bonds ($-\text{NH}\cdots\text{Si}-\text{OH}$), validated by

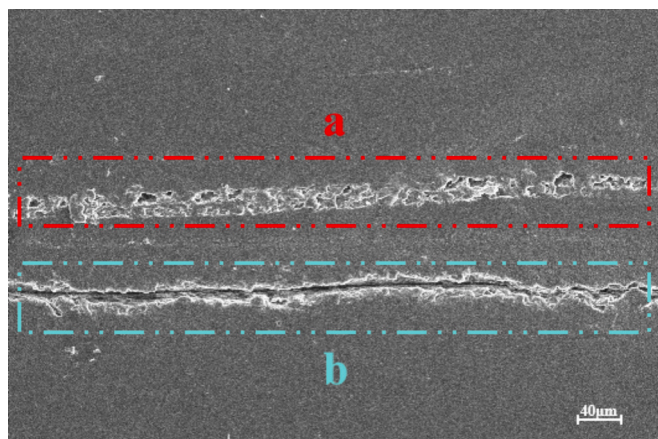


Fig. 6. FESEM images of representative scratches on MSO/Aurea-SI-5 composite coating under identical preparation conditions: (a) After 24 h of self-healing; (b) Immediately after damage (unrepaired state). All scratches were prepared with a diamond indenter (500 g load) at 25°C and 60% RH, with a consistent initial depth of $20.3 \pm 1.2\ \mu\text{m}$. The morphological differences confirm the self-healing effect, which is cross-validated by the $\sim 85\%$ depth reduction quantified on the same scratch via laser confocal microscopy (Fig. 7). Mag = 200 $\times$, WD = 11.0 mm, EHT = 10.00 kV, Signal A = SE2.

FTIR, facilitate molecular reorganization; (2) MSO released from nanoscale pools fills cracks via capillary action, forming a hydrophobic barrier. This synergy can enhance sustained self-healing and corrosion resistance of the composite coatings.

To further visually characterize the dynamic evolution of coating damage self-healing behavior at the macroscopic scale, the MSO/Aurea-SI-X coating's self-healing process was macroscopically evaluated using a laser scanning confocal microscope. Non-contact scanning (Z-resolution: $0.1\ \mu\text{m}$; wavelength: 488 nm) was employed to avoid interference during in situ creation and monitoring of biomimetic scratches (depth: $20.3 \pm 1.2\ \mu\text{m}$) within 0–48 h post-damage. As shown in Fig. 7, all coatings exhibited self-healing capabilities, with healing efficiency progressively enhanced as Urea-SI content increased. This was visually manifested through the morphological transition from initial sharp edges (85° edge angle) to blurred edges (50° edge angle) after 48 h, with complete scratch closure achieved. This visual evidence substantiates the synergistic repair mechanism: MSO molecules ($\gamma_d = 21.8\ \text{mN/m}$) released from nanoscale reservoirs (5–50 nm) effectively filled cracks via capillary action, while dynamic hydrogen bond recombination ($-\text{NH}/\text{Si}-\text{OH}$) facilitated molecular-level structural recovery.

3.3. Corrosion resistance analysis and mechanism investigation of MSO/Aurea-SI composite coatings

To systematically evaluate the anti-corrosion efficacy of MSO/Aurea-SI composite coatings on metallic substrates, different formulations of these coatings were applied to steel test panels. The coated panels were then immersed in a 3.5 wt% NaCl solution—a setup designed to simulate marine and high-salinity corrosive environments. Subsequently, the corrosion behavior and protective mechanisms of the MSO/Aurea-SI coated samples were investigated via Tafel polarization curve measurements and electrochemical impedance spectroscopy (EIS). The primary objective of this study was to elucidate the structure–activity relationship between the MSO/Aurea-SI content and the corrosion protection performance of the coatings.

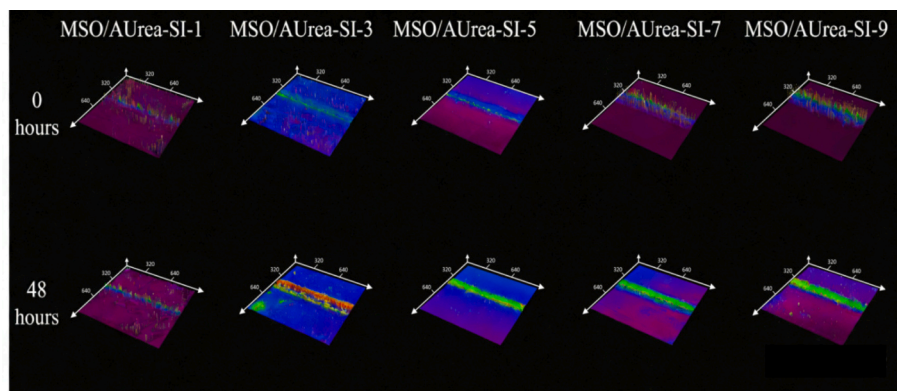


Fig. 7. Laser confocal images of post-damaged(0 h) and repaired(48 h) coating-MSO/Aurea-SI-X.

3.3.1. Tafel polarization curve

Fig. 8 presents the potentiodynamic polarization curves of the MSO/Aurea-SI-X composite coatings after 27 days of immersion in a 3.5 wt% NaCl solution. It is important to note that, due to the highly resistive nature of the organic coatings, the corrosion process is not under activation control; therefore, Tafel extrapolation is not applied for quantitative analysis of corrosion current densities [30]. The curves are discussed here solely for qualitative and comparative purposes regarding the coatings' barrier performance. A distinct positive shift in the corrosion potential (E_{corr}) is observed as the Urea-SI content increases from 1 to 5 wt%. This trend qualitatively indicates an enhanced suppression of the anodic metal dissolution reaction, suggesting a more effective barrier against electrolyte ingress for the MSO/Aurea-SI-5 formulation. Furthermore, at a constant anodic overpotential (e.g., +200 mV vs. the open-circuit potential), the MSO/Aurea-SI-5 coating exhibits the lowest anodic current density among the series, providing a direct visual comparison of its superior protective property. For coatings with higher Urea-SI loadings (7 and 9 wt%), a negative shift in E_{corr} and a significant increase in current density are evident, indicating compromised barrier integrity likely due to phase separation.

3.3.2. EIS measurements

To rigorously assess the long-term barrier performance of the MSO/Aurea-SI-X composite coatings, electrochemical impedance spectroscopy (EIS) was conducted in a 3.5 wt% NaCl solution over a 27-day immersion period (Fig. 9). Following established best practices for evaluating organic coatings on metals [31], the low-frequency

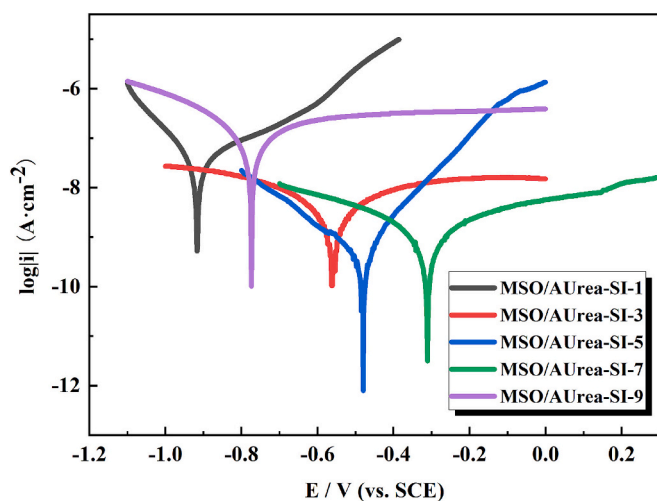


Fig. 8. Polarization curves of the different MSO/Aurea-SI-X composite coatings after being immersed in corrosive media for 27 days.

impedance modulus ($|Z|_{0.01\text{Hz}}$) and the shape of the phase angle plots were prioritized as primary, model-free indicators of coating integrity, rather than relying solely on fitted parameters from equivalent electrical circuits (EECs), which can be non-unique or physically ambiguous for complex, multi-phase systems like ours [32]. It should be noted that the impedance modulus measured by electrochemical impedance spectroscopy (EIS) is affected by multiple factors, including coating thickness, substrate condition, and test parameters. Its absolute value is not an intrinsic property of the coating material. All comparative experiments in this study were performed under strictly consistent substrate preparation, coating application, curing procedure, and electrochemical test conditions. Therefore, the impedance values reported below and their evolution over time are mainly used to evaluate the relative barrier performance and degradation rate among different MSO/Aurea-SI-X formulations within the present experimental system, so as to reveal the intrinsic relationship between composition, structure, and properties.

All coated samples exhibited initial $|Z|_{0.01\text{Hz}}$ values exceeding $10^8 \Omega\cdot\text{cm}^2$ (Table S2), confirming excellent as-prepared barrier properties. Over time, a clear composition-dependent trend emerged. The MSO/Aurea-SI-5 coating demonstrated superior stability, maintaining $|Z|_{0.01\text{Hz}} > 7 \times 10^9 \Omega\cdot\text{cm}^2$ even after 27 days of immersion. In stark contrast, both lower (1–3 wt%) and higher (7–9 wt%) Urea-SI loadings showed a significantly accelerated decay in impedance, indicating a compromised barrier function.

This superior performance of the 5 wt% formulation is further corroborated by its phase angle behavior. Throughout the entire immersion period, the MSO/Aurea-SI-5 coating displayed a single, broad time constant spanning nearly the full frequency range, with a maximum phase angle close to -80° . This signature is characteristic of a homogeneous, highly resistive, and pore-free organic coating [33]. Critically, no secondary time constant at low frequencies or a Warburg-type diffusion tail was observed, which strongly suggests the absence of electrolyte penetration to the metal/coating interface and the lack of active corrosion processes.

For the other formulations, the EIS response evolved differently. After 27 days, the Nyquist plots for MSO/Aurea-SI-1 and MSO/Aurea-SI-9 developed a second capacitive loop at low frequencies, and their Bode phase angle plots showed a distinct second time constant. This evolution is a well-documented indicator of water uptake, coating delamination, and the onset of interfacial corrosion [34]. While equivalent circuit models can provide mechanistic insights into corrosion behavior, their application requires careful interpretation for complex composite coating systems [34]. For the **initial intact stage** (0 day of immersion), a simple R(QR) equivalent circuit (Fig. 10a, where R1 denotes the solution resistance, Q1 is a constant phase element (CPE) representing the coating capacitance, and R2 is the coating resistance (R_{coat})) yielded a good fit for all coated samples. For the **intermediate corrosion stage** (Fig. 10b), the corrosive medium gradually permeates

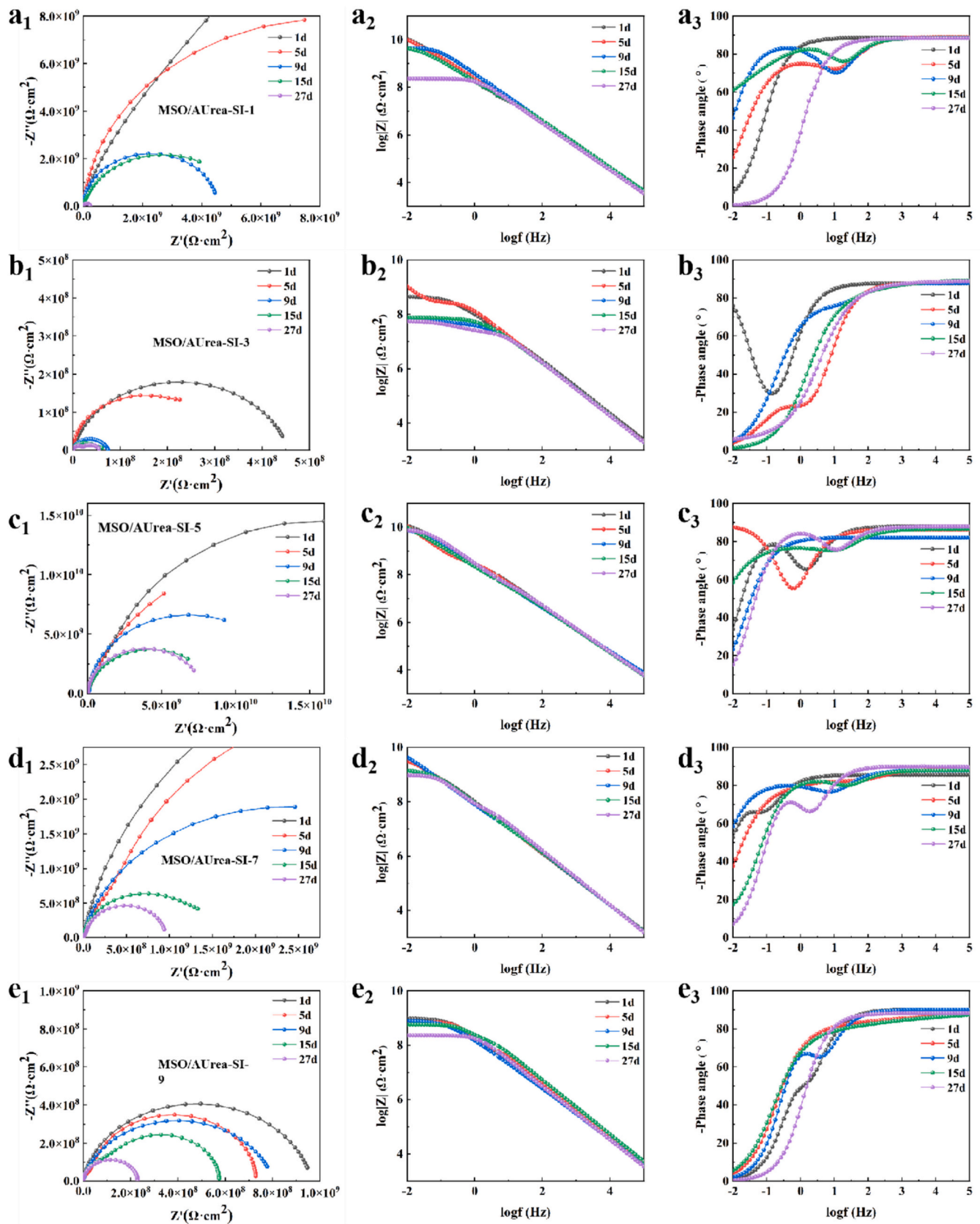


Fig. 9. Evolution of Electrochemical Impedance Behavior for MSO/AUrea-SI-X composite coatings during Prolonged Corrosion Exposure(27d) (a)MSO/AUrea-SI-1; (b) MSO/AUrea-SI-3; (c) MSO/AUrea-SI-5; (d)MSO/AUrea-SI-7; (e) MSO/AUrea-SI-9; (a1 ~ e1) Nyquist; (a2 ~ e2)Bode magnitude; (a3 ~ e3) phase angle representations.

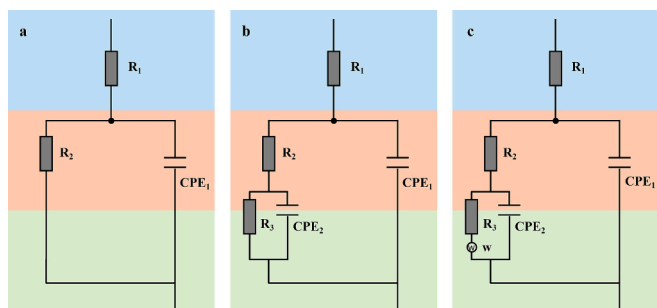


Fig. 10. The equivalent circuits used to fit the EIS results of MSO/AUrea-SI-X composite coatings in different stages: (a) The initial stage of corrosion; (b) The middle stage of corrosion; (c) The final corrosion stage.

through the coating and accumulates at the metal/coating interface, and the duration of this stage is a critical metric for evaluating the anticorrosion performance of the composite coatings. In contrast, for degraded samples at the **final corrosion stage** (e.g., MSO/AUrea-SI-1 and MSO/AUrea-SI-9), an additional $R(Q(RW))$ circuit branch (Fig. 10c) was required to fit the EIS data, which accounts for the charge transfer resistance (R_3), double-layer capacitance (C_2) and Warburg diffusion impedance (W) associated with the corroding metal/coating interface [35]. The presence of a Warburg impedance in electrochemical impedance spectroscopy (EIS) typically indicates that diffusion processes (e.g., oxygen transport, migration of corrosion products or electrolyte ions) have become the rate-limiting step of the corrosion reaction, a phenomenon generally accompanied by visible coating deterioration such as rust spots, blistering or interfacial delamination [24].

However, EIS is a highly sensitive technique that can detect incipient/early-stage coating degradation at the microscopic level-changes that are not yet discernible to the naked eye. Thus, visual inspection and EIS characterization are complementary: visual observation can confirm significant macroscopic deterioration, but fails to capture the initial onset of interfacial corrosion or subtle electrolyte penetration. In practical corrosion tests, a detected Warburg impedance usually indicates the occurrence of degradation that may evolve into visible coating failure with extended immersion time, even if no obvious visual defects are observed at the test time point. We emphasize that these circuits are used descriptively to capture the changing EIS features, and our primary conclusions regarding coating performance are firmly grounded in the robust, model-independent metrics of $|Z|_{0.01\text{Hz}}$ and phase angle analysis.

The long-term stability of the MSO/AUrea-SI-5 coating can be

attributed to the synergistic effects enabled by molecular-level compatibilization: (1) the covalent integration of Urea-SI enhances crosslink homogeneity and interfacial adhesion, creating a tortuous path for ion diffusion; (2) the dynamic hydrogen-bonding network dissipates stress and heals micro-defects that could serve as initiation sites; and (3) the nanoscale dispersion of MSO provides a reservoir for rapid hydrophobic sealing upon damage, preventing the establishment of continuous electrolyte pathways.

3.4. Self-healing performance and mechanism of MSO/AUrea-SI-5 coating

Furthermore, the scanning Kelvin probe force microscopy (SKPFM) technique was employed to characterize the local corrosion potential of the coating during the three stages: “intact-damaged-self-healed”. Based on the thermodynamic correlation between corrosion potential and corrosion resistance—a more positive corrosion potential indicates a lower thermodynamic tendency for anodic oxidation of the metal substrate, reduced local corrosion activity, and a stronger trend in coating corrosion resistance—the effectiveness of the self-healing process was analyzed. The results are shown in Fig. 11 [36,37].

Fig. 11(a) reveals that the local corrosion potential distribution of the undamaged self-healing coating was uniform, with the overall potential stabilized at 0.5–0.7 mV (vs. SCE). No significant low-potential regions (corrosion-active sites) were observed. This is because the pristine coating structure was dense, and nano-silicone oil was uniformly dispersed in the matrix in the form of microcapsules, effectively blocking the contact between corrosive species (e.g., Cl^- , O_2) and the metal substrate. This made local microcell reactions difficult to occur, demonstrating excellent initial anti-corrosion performance. After the coating was artificially scratched (simulating mechanical damage in practical applications), as shown in Fig. 11(b), the local corrosion potential in the damaged area shifted significantly negatively, with a distribution range of -0.8 mV to 0.1 mV (vs. SCE). This low-potential region coincided exactly with the scratch trajectory, indicating that the substrate metal was directly exposed to the corrosive medium at the damage site. The anodic oxidation reaction ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) occurred vigorously, leading to a significant increase in local corrosion activity and failure of the coating's protective performance. After 48 h, Fig. 11(c) shows that the local corrosion potential in the damaged area of the coating shifted significantly positively, recovering to 0 – 0.7 mV (vs. SCE).

The potential distribution became uniform again, and the low-potential active sites essentially disappeared. The core mechanism for

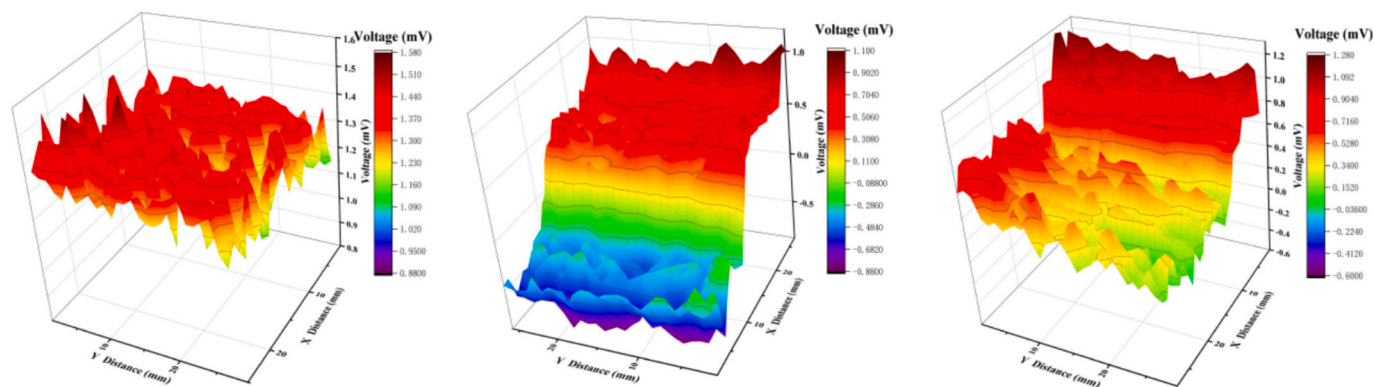


Fig. 11. SKPFM characterization of local Volta potential distribution across the self-healing coating under three distinct states: (a) intact, (b) damaged, and (c) self-healed (after 48 h). The Volta potential (contact potential difference between the coating surface and the SKPFM probe) was calibrated against a saturated calomel electrode (SCE) for comparative consistency with other electrochemical measurements (e.g., Tafel polarization, EIS) in this study. The color scale represents the calibrated local Volta potential (mV), with red/yellow indicating more noble potentials (corresponding to higher corrosion resistance) and blue indicating active regions (lower potentials, prone to corrosion). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

this change is as follows: The coating damage triggered the rupture of microcapsules, releasing the incorporated methyl silicone oil, which slowly permeated into the crack and formed a hydrophobic organic barrier film, physically blocking further penetration of corrosive species. The polar groups (e.g., ureido, hydroxyl) in the urea-modified silica sol system interacted with the functional groups of the coating matrix through hydrogen bonding, promoting the reconstruction and healing of the coating structure at the crack and reducing local defects. The combined effects of these dual actions suppressed the anodic oxidation of the substrate metal and the cathodic reduction reaction ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$), restoring the local corrosion potential to a level close to that of the intact coating [38]. This confirms that the coating achieved effective self-healing at the crack, and its anti-corrosion performance significantly recovered.

4. Conclusion

This study successfully overcomes the fundamental incompatibility between mobile healing agents and rigid polymer matrices in dual-mechanism self-healing coating systems. By molecularly engineering a urea-functionalized polysiloxane silica sol (Urea-SI) and integrating it into an acrylic resin, we achieved nanoscale compatibilization that fulfills three critical design criteria simultaneously: high crosslink density for mechanical robustness, dynamic hydrogen bonding for autonomous structural recovery, and homogeneous dispersion of methyl silicone oil (MSO) as sub-100 nm reservoirs for extrinsic sealing.

The optimal formulation (5 wt% Urea-SI) demonstrated a high and stable barrier performance, maintaining a high impedance modulus ($|Z|_{0.01\text{Hz}} > 10^9 \Omega \cdot \text{cm}^2$) for 27 days in a 3.5 wt% NaCl solution and exhibiting rapid self-healing of scratches. This is attributed to a synergistic mechanism: covalent integration enhances interfacial adhesion, dynamic H-bonds heal micro-damage, and nanoscale MSO reservoirs provide immediate hydrophobic sealing. This work establishes a generalizable molecular design principle—using multifunctional compatibilizers with dynamic bonding motifs—for developing high-performance, autonomously self-healing coatings for demanding applications.

CRedit authorship contribution statement

Zihan Lin: Writing – original draft, Investigation. **Xiao Wang:** Conceptualization. **Wei Lu:** Funding acquisition. **Fan Yang:** Formal analysis. **Zhi Liu:** Methodology. **Kunyang Zhou:** Software. **Benqing Li:** Resources. **Haohan Huang:** Validation. **Congcong Zhang:** Visualization. **Weili Li:** Writing – review & editing, Project administration.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2026.110119>.

Data availability

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

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