

Green robust superhydrophobic composite coatings based on silicone-modified corn straw fiber and hydrophobic SiO₂ for durable corrosion protection

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ARTICLE INFO

Keywords:

Superhydrophobic coating
Corn straw fiber
Silicone modification
Synergistic reinforcement
Long-term corrosion resistance
Mechanical durability

ABSTRACT

Metallic corrosion severely threatens service safety and causes substantial economic losses in marine, transportation, and chemical engineering fields. Organic anticorrosive coatings are widely applied but suffer from inherent microdefects, insufficient barrier property, and poor durability. Superhydrophobic coatings can repel corrosive media via air-layer trapping; however, their poor mechanical robustness, weak interfacial adhesion, and rapid degradation under harsh environments restrict practical applications. Herein, a green, robust, and long-lasting superhydrophobic composite coating (ACR/SiO₂-SF) was developed by using silicone oil-modified corn straw fiber (SF) and hydrophobic nano-SiO₂ as synergistic fillers in acrylic resin (ACR). Corn straw was first alkali-activated to expose hydroxyl groups and then modified via hydrosilylation to obtain hydrophobic SF with improved interfacial compatibility. Effects of SF loading on wettability, morphology, adhesion, mechanical durability, and corrosion resistance were systematically investigated. Results showed that the optimized ACR/SiO₂(20)-SF(5) coating achieved a water contact angle (WCA) of 158.14° and sliding angle (SA) of 2°, exhibiting superior superhydrophobicity, self-cleaning, and multi-liquid non-wettability. The coating reached Grade 0 cross-cut adhesion and maintained superhydrophobicity after sandpaper abrasion, water jet impact, strong acid/alkali immersion, thermal-oxidative aging, UV aging, and 90-day saltwater soaking with performance attenuation below 3%. Electrochemical impedance spectroscopy revealed that the low-frequency impedance modulus remained above 10⁹ Ω cm² after 90-day immersion in 3.5 wt% NaCl solution. The excellent long-term anticorrosion was attributed to the triple-synergy mechanism: surface superhydrophobic repellency, internal labyrinthine barrier, and long-term structural stability. This work provides a low-cost, eco-friendly, and high-performance strategy for metal corrosion protection and promotes high-value utilization of agricultural waste biomass in advanced anticorrosive coatings.

1. Introduction

Metallic components deployed in marine engineering, transportation infrastructure, and chemical processing equipment inevitably suffer severe corrosion degradation under the coupled actions of moisture, chloride ions, acid, and alkali environments [1–4]. Such corrosion not only drastically shortens service life but also causes substantial economic losses and potential safety hazards [5]. Organic coating protection has become the most widely used strategy owing to its facile

fabrication, favorable substrate compatibility, and superior barrier performance [6]. However, conventional pure resin coatings inevitably generate inherent micropores and pinholes during curing, which provide rapid diffusion pathways for water, oxygen, and corrosive ions, resulting in insufficient long-term corrosion resistance [7–9].

To improve barrier properties and durability, incorporating micro/nano functional fillers to construct composite coatings has been established as an effective approach [10]. Among various functional systems, superhydrophobic coatings (static water contact angle (WCA) > 150°;

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<https://doi.org/10.1016/j.porgcoat.2026.110459>

Received 5 May 2026; Received in revised form 27 June 2026; Accepted 18 July 2026

Available online 29 July 2026

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sliding angle(SA) $< 10^\circ$) have attracted intensive interest, as they can form a stable air layer at the solid–liquid interface that physically repels corrosive media [11,12]. The fabrication of superhydrophobic surfaces generally requires simultaneous integration of hierarchical micro/nano roughness and low-surface-energy components [13,14]. To date, numerous superhydrophobic coating systems have been developed; however, most suffer from inherent bottlenecks including poor mechanical robustness, insufficient interfacial adhesion, and rapid performance degradation under prolonged harsh environments, which severely limit practical application in corrosion protection [15,16].

In recent years, biomass-derived materials have emerged as a research focus in functional coatings owing to abundant sources, low cost, biodegradability, and environmental compatibility [17–19]. Crop straw fibers, as representative natural biomass, possess inherent microscale fibrous morphology and high specific surface area, enabling applications as reinforcing fillers and roughness-forming components [20–22]. Pyo et al. [23] employed glass fiber membranes and prepared hydrophobic surfaces via dip-coating with pure polydimethylsiloxane (PDMS), which significantly enhanced surface hydrophobicity and showed promising potential in membrane distillation. However, unmodified natural fibers are intrinsically hydrophilic and exhibit poor compatibility with hydrophobic polymer matrices, readily inducing interfacial defects, filler agglomeration, and performance deterioration [24–26]. Accordingly, hydrophobic modification of biomass fibers represents a critical prerequisite for effective application in superhydrophobic composite coatings.

Silicone-based materials, particularly PDMS and silicone oils, exhibit extremely low surface energy, excellent flexibility, thermal stability, and chemical inertness, and are thus ideal candidates for hydrophobic functionalization [4]. Zhang et al. [28] fabricated a highly durable superhydrophobic coating using PDMS as the matrix and quartz@SiO₂ composite particles as functional fillers. The coating retained superhydrophobicity even after 100 cycles of sandpaper abrasion, demonstrating outstanding mechanical robustness and wear resistance. The PDMS matrix not only contributed low surface energy but also improved interfacial bonding between fillers and resin. Xu et al. [29] developed a durable superhydrophobic TiO₂/fluorinated graphene composite coating, which achieved efficient antifouling and mechanical stability through synergistic combination of hierarchical micro/nano morphology and low-surface-energy chemistry. These studies confirm that silicone modification and multi-component synergistic assembly can significantly improve durability and stability of superhydrophobic coatings.

At present, a common strategy for constructing superhydrophobic coatings relies on single-component nanofillers (e.g., nano-SiO₂, nano-TiO₂) to create surface roughness [30,31]. Lu et al. [32] prepared a transparent superhydrophobic coating using fluorosilane-modified SiO₂ nanoparticles and waterborne polyurethane, which exhibited excellent self-cleaning and antibacterial properties, although mechanical durability required further improvement. Single nanofillers are prone to severe agglomeration, which increases coating defects and degrades both transparency and mechanical performance [33]. In contrast, micro-nano synergistic systems composed of microscale fibers and nanoparticles can form interpenetrating network structures, which not only optimize hierarchical roughness but also enhance mechanical strength and barrier properties [34]. However, relatively few studies have systematically investigated the synergistic strengthening mechanism of silicone-modified agricultural waste fibers and hydrophobic nano-SiO₂ within an acrylic resin matrix, especially with regard to long-term corrosion resistance and stability under simulated marine environments.

Against this background, the present work employs corn straw, a typical agricultural waste, as raw material. Alkali activation is first performed to remove lignin and hemicellulose, exposing abundant active hydroxyl groups and increasing fiber specific surface area. Vinyl silicone oil and hydrogen-containing silicone oil are then grafted onto fiber surfaces via hydrosilylation to produce silicone-SF (SF) with

improved hydrophobicity and interfacial compatibility. Furthermore, SF and hydrophobic nano-SiO₂ are used as composite fillers, and acrylic resin (ACR) serves as the film-forming matrix to construct ACR/SiO₂-SF superhydrophobic composite coatings.

The influences of SF loading on wettability, surface morphology, and interfacial adhesion are systematically investigated. Mechanical durability (sandpaper abrasion, water jet impact), chemical stability (strong acid, strong alkali), and environmental stability (3.5 wt% NaCl solution immersion, thermal-oxidative aging) are comprehensively evaluated. Long-term corrosion resistance is assessed via 90-day electrochemical measurements. This study focuses on revealing the synergistic strengthening mechanism between SF and nano-SiO₂, as well as the triple-synergy corrosion protection mechanism comprising “surface superhydrophobic repellency, internal physical barrier, and long-term structural stability”. The work not only realizes high-value utilization of agricultural waste corn straw but also provides a feasible strategy for preparing low-cost, eco-friendly, mechanically robust, and long-lasting corrosion-resistant superhydrophobic coatings, thereby possessing important theoretical significance and engineering application value. Given that the developed superhydrophobic coating is designed as a functional topcoat for long-term outdoor and marine service, acrylic resin (ACR) is selected as the film-forming matrix instead of epoxy resin. Although epoxy resin possesses excellent barrier property and substrate adhesion, its poor UV resistance and tendency toward yellowing and chalking under prolonged weathering greatly limit its application as an outdoor topcoat. In contrast, acrylic resin features outstanding weatherability, reliable gloss retention and wide acceptance in industrial anti-corrosion topcoat formulations, and exhibits good compatibility with silicone-modified biomass fibers and hydrophobic silica nanoparticles, enabling room-temperature curing and scalable fabrication.

2. Experimental section

2.1. Materials

Corn straw was collected from local farmlands. After manual harvesting, the raw material was subjected to sequential pretreatment steps including removal of impurities, washing, drying, crushing and sieving, to obtain a particle size range of 200–500 mesh. The resulting powder was dried and stored in a sealed container for subsequent use.

One-component acrylic resin Macrynal™ T 5015 was supplied by Allnex. Analytical grade chemical reagents including sodium hydroxide (NaOH, $\geq 96\%$), butyl acetate, vinyl silicone oil (MK-VS1000, vinyl content: 0.10 ± 0.01 wt%), hydrogen-containing silicone oil (MK-HS500, active hydrogen content: 0.50 ± 0.02 wt%) and Platinum catalyst (Karstedt's catalyst, platinum content: 3000 ppm in vinyl silicone oil) were purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Hydrophobic fumed silica R972(BET specific surface area: 110 ± 20 m²/g, Average primary particle size: approx. 16 nm) was obtained from Evonik Industries. Wetting and dispersing agent BYK® Disperbyk-110 was provided by BYK-Chemie GmbH (Wesel, Germany). All reagents and solvents were used as received without further separation or purification. Distilled water used in all the experiments was prepared in the laboratory.

2.2. Preparation of silicone oil-modified corn straw Fiber (SF)

At first, the corn straw powder was immersed in a 10 wt% aqueous NaOH solution and magnetically stirred at a constant temperature of 80 °C for 2 h. After the reaction, the product was rinsed repeatedly with distilled water until the washing solution reached a neutral pH. The resulting sample was freeze-dried and then sieved through a 100-mesh sieve to obtain alkali-treated corn straw fiber, denoted as ACF.

Then, 10 g dried ACF powder was uniformly dispersed in 100 mL butyl acetate serving as the dispersion medium. Vinyl silicone oil (MK-VS1000) and hydrogen-containing silicone oil (MK-HS500) were

blended at a fixed mass ratio of vinyl silicone oil: hydrogen-containing silicone oil = 3:1, and the total mass of mixed silicone oils was controlled at 2 g, achieving a mass ratio of ACF to total mixed silicone oil of 5:1. Karstedt's platinum catalyst (3000 ppm platinum stock solution) was added into the mixed system at a dosage of 50 ppm Pt relative to the total mass of vinyl and hydrogen-containing silicone oil. After catalyst addition, the mixture was slowly heated to 120 °C and allowed to react for 5 h under continuous magnetic stirring at 300 rpm. During the reaction, organosilicon compounds underwent hydrosilylation and adsorbed preferentially on the surface of ACF fibers to form a hydrophobic crosslinked coating. Subsequently, the resulting product was isolated by centrifugation at 8000 r/min for 10 min, washed twice with fresh butyl acetate to remove unreacted silicone oil residues, and freeze-dried at -50 °C for 24 h to obtain silicone oil-modified corn straw fiber, designated as SF.

2.3. Preparation of ACR/SiO₂(X)-SF(Y) Superhydrophobic composite coatings

With the assistance of wetting agent BYK Disperbyk-110, hydrophobic fumed silica R972 was added to the acrylic resin matrix at a dosage of 25 wt% relative to the solid content of the acrylic resin (ACR), i.e., Macrynal™ T 5015. The mixture was first subjected to ultrasonic dispersion, followed by further homogenization via high-speed grinding and stirring, thus preparing a uniformly dispersed acrylic resin/silica (ACR/SiO₂) suspension.

To systematically investigate the regulatory effect of the addition amount of SF on the properties of ACR/SiO₂ composite coatings, a SF dispersion with a solid content of 10 wt% was first prepared and ultrasonically dispersed for 15 min. Subsequently, the SF dispersion was added into the aforementioned ACR/SiO₂ suspension at different proportions, with the addition amount of SF controlled in the range of 1–6 wt% relative to the mass of Macrynal™ T 5015. The resultant mixture was then mechanically stirred for 15 min to obtain a homogeneously dispersed composite coating. For the clear differentiation of samples with different formulations, the prepared composite coatings were designated as ACR/SiO₂(X)-SF(Y) (where X represents the mass percentage of SF relative to Macrynal™ T 5015).

To examine the cross-sectional morphology of the coatings and explore the correlation between morphology and the properties of the cured coatings, Q235 steel plates and silica glasses were utilized as substrates and coated with different ACR/SiO₂(X)-SF(Y) paints at room temperature. Before coating, the steel panels were polished with sandpaper and subsequently cleaned with alcohol to remove dust. The coatings were allowed to dry at room temperature for 7 days (168 h), with the thickness of the coatings being controlled at 90 μm on steel panels and 30 μm on silica glasses.

2.4. Structural and characterizations

Fourier transform infrared (FTIR) spectroscopy analysis of the SF-modified fiber powder was conducted on a Nicolet iS10 FTIR spectrometer (Thermo Electron Corporation, USA) with the spectra recorded in the range of 4000–500 cm⁻¹ at a resolution of 4 cm⁻¹, and the effect of silicone oil surface modification on its thermal resistance was characterized by a thermogravimetric/differential thermal analyzer (TG/DTA, Diamond Series, PerkinElmer), while the surface chemical composition of the SF-modified fiber powder was analyzed via X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, USA). The surface micromorphologies of the SF-modified fiber powder and the resultant ACR/SiO₂-SF coatings were observed using a field emission scanning electron microscope-energy dispersive spectroscopy (FESEM-EDS) system (S4700, Hitachi, Japan), with the surface elemental composition and distribution determined by the EDS accessory. The water contact angle (WCA) and sliding angle (SA) of the ACR/SiO₂-SF coatings was measured by an optical contact angle meter

(Attension Theta Flex, Biolin Scientific, Sweden) via the sessile drop method, and the corrosion resistance of the cured composite coatings was evaluated on a CHI660A electrochemical workstation through electrochemical impedance spectroscopy (EIS) analyses. The interfacial durability and stability of the ACR/SiO₂-SF coatings were comprehensively assessed including mechanical durability, adhesion, chemical stability, salt water resistance, UV aging resistance and thermal stability, where the mechanical durability was tested by sandpaper abrasion and water jet impact: the sandpaper abrasion test was performed by rubbing the coatings at a constant speed on 1000-mesh silicon carbide sandpaper under a 500 g load with a single abrasion distance of 20 cm and the WCA recorded every 5 cycles, and the water jet impact test was carried out by spraying water at a velocity of 9 m/s onto the coatings horizontally inclined at 45° and placed 50 cm below the water outlet; the adhesion was evaluated according to the cross-cut test standard (ISO 2409:2020); the chemical stability was determined by immersing the coatings in a strong acid solution (pH = 1) for 48 h and a strong alkali solution (pH = 14) for 24 h followed by WCA measurements; the salt water resistance was tested by immersing the coatings in a 3.5 wt% NaCl aqueous solution for 90 d and then measuring the WCA; the thermal stability was assessed by placing the coatings at 120 °C for 7 d and determining the corresponding WCA.

3. Results and discussion

3.1. Structural and performance analysis of modified Fiber SF

3.1.1. FTIR measurement

FTIR spectroscopy was conducted on raw CF and silicone oil-modified fiber (SF) to investigate the evolution of surface functional groups and verify the hydrosilylation grafting reaction, with results shown in Fig. S1.

FTIR analysis showed that raw CF exhibited a strong and broad -OH stretching band at 3300–3500 cm⁻¹ (centered at 3412 cm⁻¹) from cellulose, hemicellulose, and residual lignin. After silicone modification, the corresponding peak for SF shifted to 3442 cm⁻¹ with lower intensity and narrower width, primarily due to the physical shielding effect of the crosslinked silicone layer, accompanied by minor dehydrogenation and hydrogen bond rearrangement. The weak C-H stretching band of CF at 2810 cm⁻¹ was enhanced and sharpened to 2829 cm⁻¹ in SF, confirming the successful introduction of Si-CH₃/Si-CH₂- groups via hydrosilylation. No residual Si-H or C=C peaks were observed in SF, indicating complete reaction of active groups. The characteristic peak of CF at 1601 cm⁻¹, assigned to overlapping C=O and C=C stretching, remained almost unchanged at 1600 cm⁻¹ for SF, proving that the fiber skeleton was well preserved without degradation or side reactions. In the 1500–1000 cm⁻¹ range, the C-H in-plane bending peak of CF shifted from 1363 to 1359 cm⁻¹ with slight broadening for SF, and the polysaccharide C-O-C-O-C band was significantly broadened to 1080 cm⁻¹ due to the overlap with Si-O-Si asymmetric stretching, providing direct evidence for successful silicone grafting. The absence of an obvious Si-O-C peak confirmed that hydrosilylation cross-linking, rather than direct covalent bonding between silicone oil and fiber -OH groups, was the main modification pathway. In summary, FT-IR results confirmed the formation of a continuous organosilicon coating on CF via complete hydrosilylation with no residual active groups. The physical shielding of the modified layer and characteristic absorption of grafted groups jointly led to reduced -OH absorption, enhanced alkyl absorption, broadened Si-O-Si peaks and emerging silicone oil characteristic peaks in the fingerprint region, comprehensively verifying the successful silicone oil grafting modification of CF.

3.1.2. FESEM and EDS measurement

FESEM combined with EDS measurement was employed to systematically investigate the morphological evolution of raw CF during each modification stage and the interfacial adhesion characteristics of the

modified layer, with the results presented in Fig. 1a~g. As-received CF exhibited a regular rod-like morphology, whose surface was covered by a dense lignin-hemicellulose composite coating. The fiber surface was relatively smooth with scarce active hydroxyl sites and a low specific surface area (Fig. 1a), resulting in poor interfacial compatibility with organic polymer matrices. After alkaline treatment, obvious etching and spalling occurred on the fiber surface, forming a porous and rough texture with dissociated fiber bundles observed in local areas (Fig. 1b). This phenomenon was mainly attributed to the selective dissolution of lignin and hemicellulose on the fiber surface by alkaline solution, which not only successfully exposed the cellulose microfibrils inside the fiber, but also significantly increased the fiber specific surface area and introduced numerous active hydroxyl sites, thus constructing a sufficient reaction interface for subsequent silicone oil grafting modification. After the synergistic modification with vinyl silicone oil and hydrogen-containing silicone oil, the fiber surface was completely covered by a continuous wrinkled organosilicon coating, and the rough etched morphology formed by alkaline treatment was effectively modified with only the intrinsic rod-like outline of the fiber retained (Fig. 1c). This indicated that the two types of silicone oil were successfully grafted and coated on the fiber surface via hydrosilylation reaction, which not only endowed the fiber with low surface energy siloxane segments, but also significantly improved its interfacial compatibility with the ACR matrix.

The modification effect of the fiber was further verified by EDS elemental mapping analysis (Fig. 1d~g). Fig. 1d is a magnified FESEM image of the modified fiber (SF) in Fig. 1c, which clearly reveals the microstructural details of the wrinkled organosilicon coating on its surface. The elemental distribution results showed that silicon element was uniformly and continuously distributed on the fiber surface (Fig. 1g), providing direct evidence for the successful adhesion of the organosilicon modified layer. In addition, the distribution characteristics of oxygen and carbon elements (Fig. 1e, f) corresponded to the hydroxyl structure of cellulose in the fiber matrix and the inorganic skeleton of siloxane and alkyl carbon chain structure in the modified layer, respectively, which further confirmed that the modification reaction between silicone oil and fiber proceeded smoothly.

3.1.3. XPS Measurement

The survey XPS spectrum of SF (Fig. S2 a) displays three prominent

characteristic peaks at 284.8 eV, 532.8 eV, and 102 eV, corresponding to C 1s, O 1s, and Si 2p, respectively, with the clear emergence of the Si 2p signal directly confirming the successful introduction of silicon species and effective immobilization of polysiloxane on the fiber surface. For the high-resolution C 1s spectrum (Fig. S2 b), deconvolution reveals three distinct components: the dominant peak at 284.8 eV is assigned to C–C/C–H bonds, originating primarily from abundant methyl groups ($-\text{CH}_3$) in the polysiloxane framework and alkyl chains ($-\text{CH}_2-\text{CH}_2-$) formed via hydrosilylation, which confirms the fiber surface is covered by an alkyl-rich hydrophobic organosilicon layer; the peak at 286.3 eV corresponds to inherent C–O bonds (hydroxyl and ether linkages) from the native CF matrix; and a new characteristic peak at 284.0 eV is attributed to C–Si bonds from $\text{Si}-\text{CH}_3$ and $\text{Si}-\text{CH}_2-\text{CH}_2-$ moieties in the grafted polysiloxane, providing direct evidence for successful organosilicon loading. The high-resolution O 1s spectrum (Fig. S2 c) is curve-fitted into two components, with a dominant peak at 532.2 eV ascribed to Si–O–Si bonds that form the backbone of the crosslinked polysiloxane network, and a weaker secondary peak at 532.8 eV corresponding to C–O bonds from the underlying fiber matrix, while the high-resolution Si 2p spectrum (Fig. S3 d) is resolved into two peaks: the principal peak at 102.2 eV is assigned to Si–C bonds, characteristic of the $\text{Si}-\text{CH}_3$ and $\text{Si}-\text{CH}_2-\text{CH}_2-$ structures generated via hydrosilylation between vinyl silicone oil and hydrogen-containing silicone oil, and the minor peak at 103.5 eV corresponds to Si–O–Si bonds in the polysiloxane main chain. Collectively, these XPS results demonstrate that the SF surface is dominated by hydrophobic alkyl-rich polysiloxane structures, with the strong C–C/C–H and Si–C signals alongside the prominent Si–O–Si peak collectively verifying the formation of a stable polysiloxane layer on the fiber surface via hydrosilylation modification.

3.2. Effect of effective SF doping on the morphology and properties of composite coatings

Herein, the influence of R972 content on coating surface energy was systematically examined, followed by the incorporation of SF to explore synergistic effects and reinforcement mechanisms. Composite coatings were designated as ACR/SiO₂(X)-SF(Y), where X and Y represent the mass fractions of nano-SiO₂ and SF relative to ACR solid content, respectively (Fig. 2).

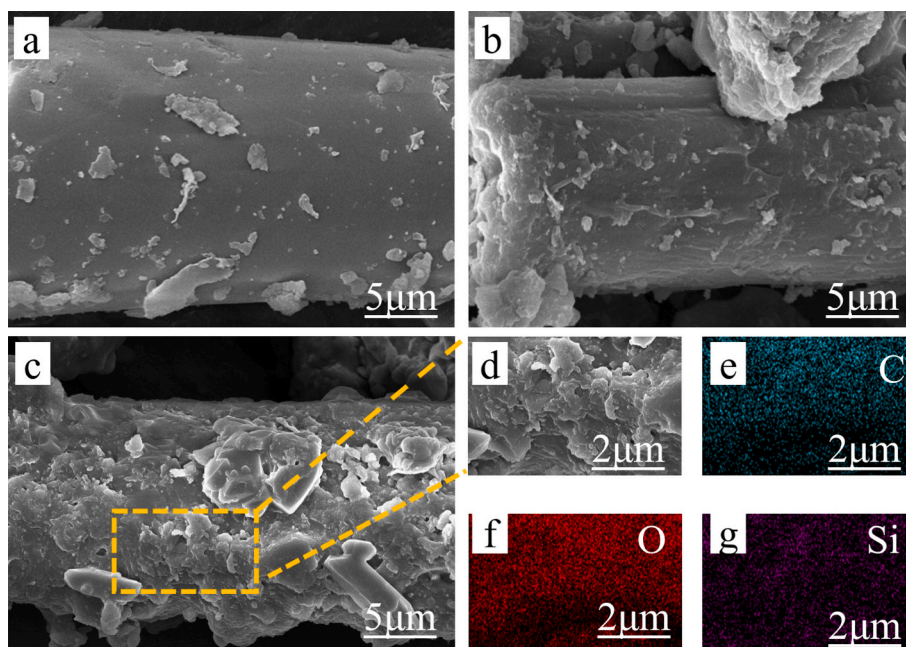


Fig. 1. FESEM images and EDS elemental mapping of CFs at different modification stages (a) Raw CF; (b) ACF; (c) SF; (d) magnified FESEM image of SF; (e–g) EDS elemental mapping of C, O and Si for SF, respectively.

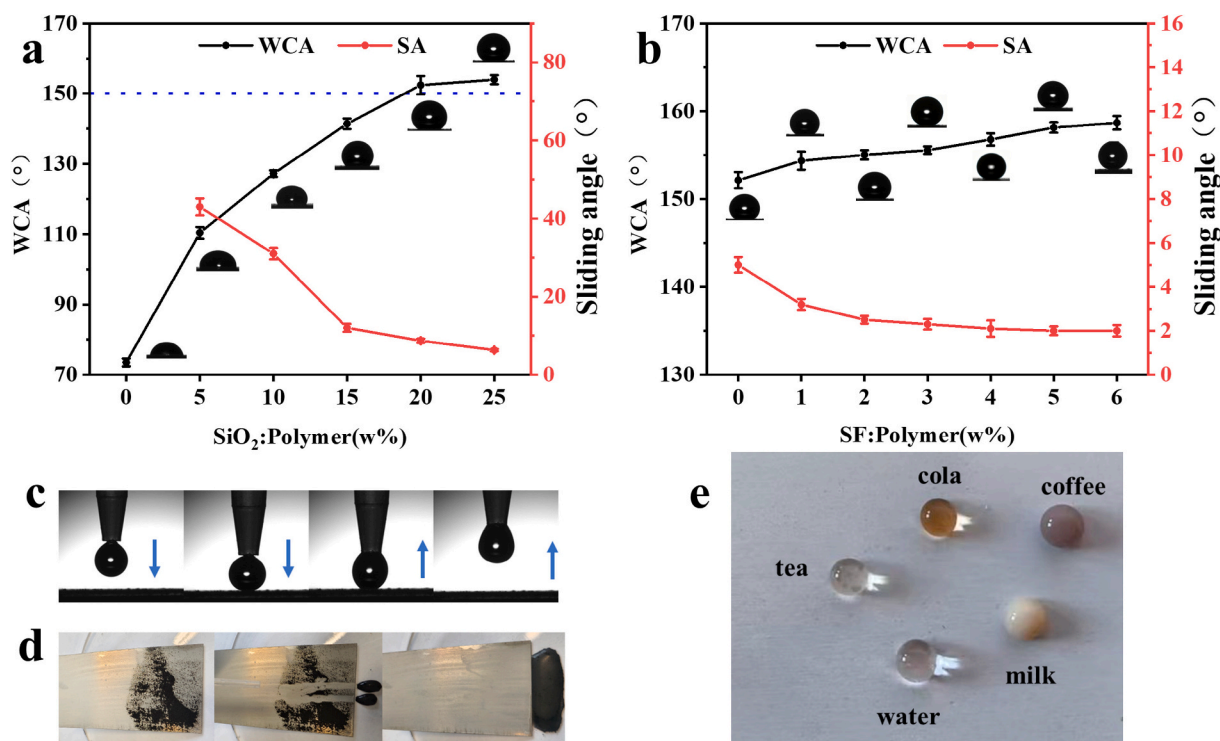


Fig. 2. (a) Effects of SiO₂ mass fraction on the WCA and SA of ACR/SiO₂ coatings; (b) effects of SF mass fraction on the WCA and SA of ACR/SiO₂(20)-SF coatings; (c) optical photographs of static WCAs for the pure ACR coating, ACR/SiO₂ composite coating, and ACR/SiO₂(20)-SF (5) composite coating; (d) optical photograph of dynamic water droplet adhesion test on the ACR/SiO₂ (20)-SF(5) coating surface; (e) antifouling property test of the ACR/SiO₂ (20)-SF (5) coating; (f) Static wetting morphologies of various daily liquids on the ACR/SiO₂(20)-SF(5) coating surface.

Neat ACR showed a WCA of approximately 73°, indicating inherent hydrophilicity caused by polar carboxyl and ester groups. With increasing R972 loading, micro/nano hierarchical roughness gradually developed via particle accumulation (Fig. 2a), significantly enhancing surface hydrophobicity. At 20 wt% SiO₂, the coating achieved superhydrophobicity with WCA > 150° and sliding SA = 8°. Further increasing SiO₂ to 25 wt% maximized WCA at ~154° and reduced SA to 7°, but excessive nanoparticles impaired resin encapsulation, weakened interfacial adhesion, and introduced structural defects. Thus, 20 wt% SiO₂ was chosen as the optimal loading to balance superhydrophobicity and film integrity.

Introduction of SF synergistically boosted wettability. The SiO₂-only coating displayed only single-scale roughness, whereas increasing SF content from 0 to 6 wt% established well-defined micro/nano hierarchical structures via microscale fiber and nanoscale silica cooperation (Fig. 2b). Low-surface-energy silicone segments on SF further reduced overall surface energy. The optimal performance achieved at 5 wt% SF, with WCA = 158.14° and SA = 2°, representing superior superhydrophobicity and dynamic dewetting behavior. No further improvement was observed above 6 wt% SF, indicating performance saturation.

Dynamic water droplet adhesion tests for ACR/SiO₂(20)-SF (5) (Fig. 2c) revealed that droplets maintained perfect spherical shapes without spreading, adhesion, or rupture during contact and retraction, confirming extremely low solid-liquid adhesion and stable Cassie-Baxter wetting. The coating exhibited excellent self-cleaning performance (Fig. 2d): carbon black contaminants were fully removed by rolling water droplets, leaving no residue. Moreover, the coating displayed universal non-wettability toward tea, water, cola, coffee, and milk, all retaining near-spherical shapes without wetting or permeation (Fig. 2e), demonstrating robust liquid repellency regardless of surface tension, viscosity, or polarity.

3.2.1. Comparison of surface and cross-sectional morphologies between conventional coatings and composite coatings

Based on the above results, pure ACR, ACR/SiO₂ (20), and ACR/SiO₂(20)-SF (5) were selected as typical samples to investigate the morphological evolution of coatings influenced by different fillers using FESEM. As shown in Fig. 3, the surface and cross-sectional micromorphologies of these coatings were systematically compared. The neat ACR coating displayed a smooth, homogeneous, and compact film without any microscale textures (Fig. 3a). In comparison, the composite coating loaded with 20 wt% SiO₂ exhibited a rougher surface; however, obvious agglomeration of SiO₂ nanoparticles could be observed in Fig. 3b and c, which weakened the uniformity of the surface structure. After further introducing 5 wt% SF (Fig. 3d and e), a uniform and continuous micro-nano hierarchical roughness was successfully constructed, in which SiO₂ agglomeration was effectively suppressed. In this hierarchical structure, microscale protrusions were provided by the exposed SF, while nanoscale roughness originated from well-dispersed SiO₂ nanoparticles. Such a lotus-leaf-like hierarchical structure enables efficient air trapping on the coating surface and stabilizes the Cassie-Baxter wetting state, thereby offering essential structural support for superhydrophobicity. The cross-sectional morphology (Fig. 3f) further confirmed that the ACR/SiO₂(20)-SF (5) composite coating possessed a dense and homogeneous internal structure, in which rod-shaped SF were uniformly embedded in the acrylic matrix with tight fiber-resin bonding and no apparent interfacial voids or defects. Owing to the spatial steric hindrance effect of the modified fibers, nano-SiO₂ was dispersed homogeneously throughout the coating, forming a reinforced-concrete-like composite structure. The improved interfacial compatibility between fibers and resin, together with the fiber-induced bridging and crack-deflection effects, contributed significantly to the enhanced mechanical robustness of the composite coating.

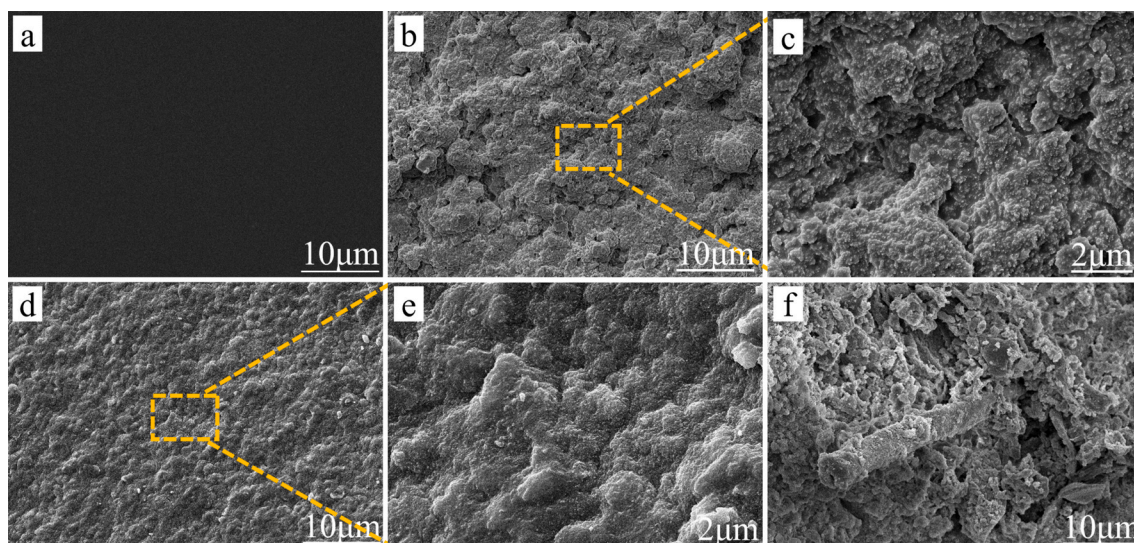


Fig. 3. FESEM images of the surface and cross-sectional morphologies of the coatings: (a) ACR Coating; (b) ACR/SiO₂ (20) Coating; (c) magnified FESEM image of ACR/SiO₂ (20); (d) ACR/SiO₂(20)-SF (5) composite coating; (e) magnified FESEM image of ACR/SiO₂(20)-SF (5); (f) cross-sectional morphology of ACR/SiO₂(20)-SF (5) coating.

3.2.2. Interfacial adhesion and mechanical properties of superhydrophobic composite coatings

Conventional superhydrophobic coatings usually incorporate a large amount of fumed SiO₂, yet these nanoparticles cannot be fully encapsulated by the polymer resin. The agglomeration of inorganic fillers further impairs the mechanical properties of the resultant coatings. Improving the mechanical performance of superhydrophobic coatings while retaining their superhydrophobicity—thus enabling real-world application—is a key focus of this work.

It is critical to distinguish two independent performance indicators: cross-cut Grade 0 adhesion characterizes the static bonding strength between the whole coating and Q235 steel substrate, which only prevents macroscopic peeling and delamination of the coating from the metal substrate; by contrast, the decay of superhydrophobicity under water jet impact and sandpaper abrasion originates from the damage and shedding of surface micro/nano rough structure, rather than coating-substrate interfacial debonding. High substrate adhesion is a necessary but insufficient condition for excellent mechanical durability, and the two properties are governed by different reinforcement mechanisms of SF.

Firstly, the interfacial adhesion between the coatings and the substrate was systematically characterized by cross-cut tests, including neat ACR coating (based on Macrynal™ T 5015), ACR/SiO₂ (20) coating, and ACR/SiO₂-SF coating (represented by ACR/SiO₂ (20)-SF (5)). The test was strictly performed in accordance with ISO 2409:2020 standards: a cross-cut cutter with a standard 1 mm grid spacing was used, with the

blade fully penetrating the coating down to the Q235 steel substrate. The adhesion grade of the coatings was evaluated according to the 0–5 grading system specified in the standards. The macroscopic morphologies of the coatings after testing are shown in Fig. 4a, b, and c. Neat ACR coating showed intact grid edges with no peeling, blistering, or delamination, and the film remained uniform, achieving Grade 0 adhesion in accordance with ISO 2409. This reflects strong interfacial bonding between polar ester groups in ACR and substrate active sites, as well as good cohesion from the crosslinked network. After cross-cut testing, the ACR/SiO₂ (20) coating exhibited severe irregular peeling, interfacial delamination at grid edges, and obvious flaking at scratch intersections, resulting in Grade 4 adhesion per ISO 2409, indicating drastically degraded adhesion. Poor compatibility between nano-SiO₂ and ACR, particle agglomeration, interfacial defects, and stress concentration disrupted the crosslinked network, reduced cohesion, and accelerated crack propagation, leading to widespread coating detachment. In contrast, the ACR/SiO₂ (20)-SF (5) composite coating retained smooth grid edges with negligible damage, no obvious peeling or delamination, and maintained Grade 0 adhesion equivalent to neat ACR, far better than ACR/SiO₂ (20).

In terms of adhesion improvement: silicone segments grafted on SF improve the compatibility among acrylic matrix, hydrophobic nano-SiO₂ and fiber, eliminate filler-matrix interfacial defects, relieve internal residual stress, and maintain the continuity of resin crosslinked network, thus avoiding large-area macroscopic film peeling from the substrate. Nevertheless, superior substrate adhesion alone cannot protect the

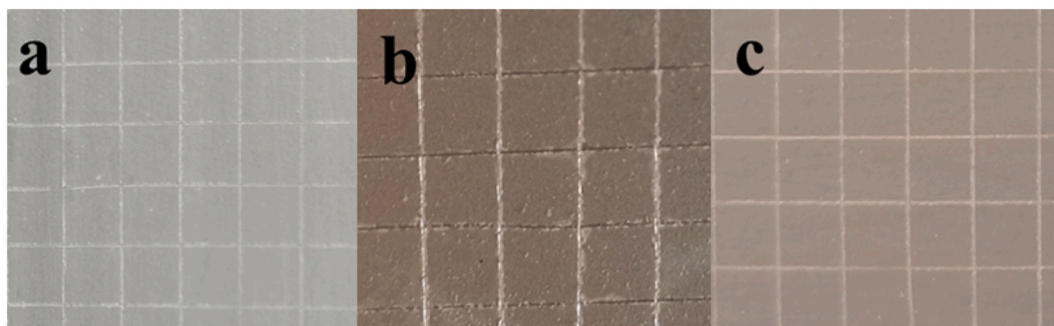


Fig. 4. Digital photographs of coatings after cross-cut adhesion test: (a) neat ACR coating, (b) ACR/SiO₂ (20) composite coating, (c) ACR/SiO₂(20)-SF (5) composite coating.

surface micro-nano rough structure under dynamic mechanical loads such as friction and high-speed water impact. The outstanding mechanical durability of ACR/SiO₂(20)-SF (5) is mainly attributed to the rigid three-dimensional interpenetrating network constructed by high-aspect-ratio SF inside the coating, rather than the promotion of substrate adhesion. The direct morphological evidence is provided in Supplementary Fig. S3a–d. After sandpaper abrasion and water jet impact, the single ACR/SiO₂ coating presents severe shedding and collapse of nano-SiO₂ particles, with the hierarchical lotus-leaf-like rough structure completely flattened and destroyed; on the contrary, SF acts as a stable supporting skeleton to anchor nano-SiO₂ uniformly in the resin matrix. The fibrous network effectively dissipates impact and shear stress, restrains the migration and detachment of SiO₂ nanoparticles, and preserves the integrated micro-nano hierarchical roughness after mechanical damage. This structural protection effect of SF on SiO₂ rough layer fundamentally maintains stable superhydrophobicity under harsh mechanical conditions. The dual optimization of Grade 0 static substrate adhesion and SF-reinforced surface structural robustness together endows the composite coating with integrated anti-delamination and anti-abrasion capacity for long-term marine service.

The exceptional interfacial adhesion stems from the multiscale synergy of SF. Silicone segments on SF improved compatibility with ACR and hydrophobic SiO₂, eliminating interfacial defects, relieving

internal stress, and preserving network continuity. Meanwhile, high-aspect-ratio fibers formed bridging and stress-transfer networks that dissipated stress, inhibited microcrack initiation and propagation, and prevented delamination. Physical entanglement and strong interfacial bonding between fibers and ACR chains further enhanced coating cohesion. Together, SF and nano-SiO₂ built a reinforced-concrete-like structure with uniform dispersion and sufficient resin encapsulation of micro/nano phases, enabling simultaneous superhydrophobic functionalization and greatly improved interfacial adhesion.

3.2.3. Mechanical robustness and environmental stability of acr/sio₂-sf superhydrophobic composite coatings

Mechanical durability of the nano-SiO₂-doped acrylic coating (ACR/SiO₂) and the SF/SiO₂ composite coating (ACR/SiO₂-SF) was systematically evaluated using ACR/SiO₂ (20) and ACR/SiO₂ (20)-SF (5) as typical samples. Water jet impact tests (impact height: 50 cm; setup shown in Fig. 5c) and linear reciprocating abrasion tests (500 g load, 20 cm per cycle; setup illustrated in Fig. 5d) were conducted. As presented in Fig. 5a, the initial WCAs of ACR/SiO₂ (20) and ACR/SiO₂ (20)-SF (5) were 152° and 158°, respectively, both meeting the superhydrophobic criterion. With increasing cumulative water impact up to 250 g, the WCA of ACR/SiO₂ (20) decreased linearly to 114°, indicating a complete

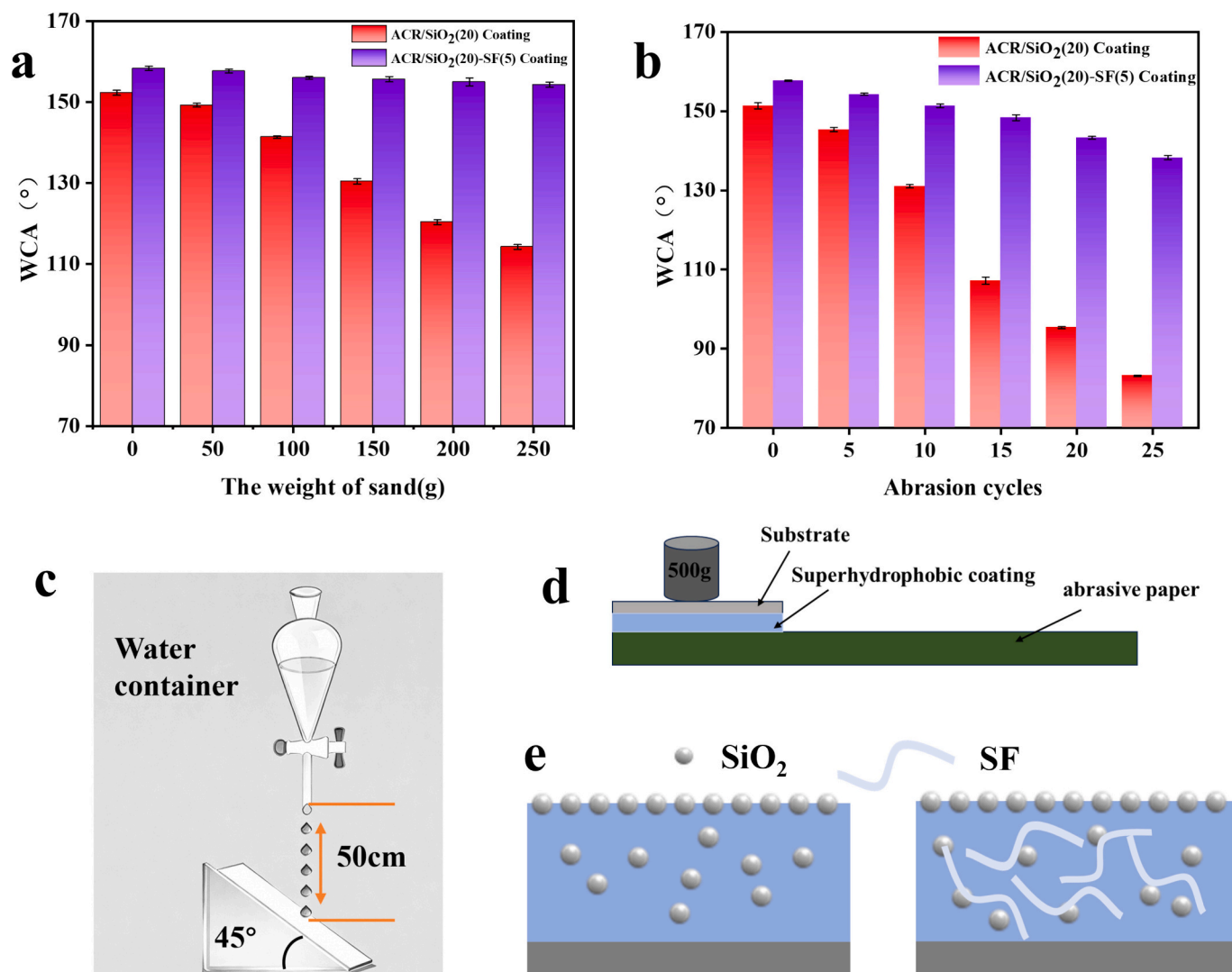


Fig. 5. WCA evolutions of ACR/SiO₂ and ACR/SiO₂-SF coatings under mechanical tests: (a) water jet impact; (b) linear abrasion cycling; (c) water jet impact setup; (d) linear abrasion setup; (e) microstructural schematic of the two coatings.

loss of superhydrophobicity. In sharp contrast, the WCA of ACR/SiO₂ (20)-SF (5) only declined slightly to 154° and remained above 150° throughout the test.

The rapid degradation of ACR/SiO₂ (20) under water jet impact arises from weak interfacial adhesion and insufficient anchoring between nano-SiO₂ and the acrylic matrix. Transient dynamic loading and shear stress caused by continuous water impact induce detachment, migration, and agglomeration of surface SiO₂ nanoparticles, rapidly destroying the micro-nano hierarchical roughness (Fig. S1a). Meanwhile, microcracks and interfacial defects form in the resin matrix, accelerating water penetration, increasing surface energy, and triggering an irreversible transition from the superhydrophobic to the hydrophilic state. In comparison, the excellent water-impact resistance of ACR/SiO₂ (20)-SF (5) is attributed to the continuous three-dimensional network formed by SF, which firmly anchors nano-SiO₂ in the resin matrix. The rigid yet tough fibers effectively dissipate impact stress, suppress matrix cracking and interfacial debonding, and thus preserve the superhydrophobic microstructure (Fig. S1b).

Linear reciprocating abrasion tests further amplified the performance difference between the two coatings (Fig. 5b). After 25 abrasion cycles, the WCA of ACR/SiO₂ (20) dropped sharply to 82°, becoming fully hydrophilic. Under combined normal loading and reciprocating shear, surface SiO₂ particles were extensively removed and the rough structure was flattened, exposing the underlying hydrophilic ACR and causing a total loss of hydrophobicity (Fig. S1c). In contrast, ACR/SiO₂ (20)-SF (5) maintained a high WCA of 138° after 25 cycles, retaining strong hydrophobicity. As evidenced by Fig. S1d, the coating preserved partial integrity of its original lotus-leaf-like hierarchical papillary microstructure after the reciprocating abrasion cycle test.

As illustrated in Fig. 5e, the significant enhancement in mechanical durability, hydrophobic stability, and structural integrity of the composite coating is fundamentally driven by the dual synergistic effects of SF and hydrophobic nano-SiO₂, realized via micro/nano-scale structural regulation and intrinsic property complementation. On one hand, the incorporation of SF effectively achieves uniform dispersion of nano-SiO₂ in the ACR matrix and inhibits the stacking and agglomeration of nanofillers. Specifically, the hydrosilylation-grafted polysiloxane chains on the SF surface possess excellent chemical compatibility with both the ACR matrix and the hydrophobic modification layer of fumed SiO₂ nanoparticles, eliminating the intrinsic interfacial incompatibility between inorganic fillers and the organic polymer matrix. Meanwhile, the high-aspect-ratio SF forms a continuous three-dimensional interpenetrating network in the coating, which provides strong spatial steric hindrance to restrict the Brownian motion and spontaneous agglomeration of high-surface-energy nano-SiO₂, thus achieving homogeneous dispersion of nanofillers and avoiding structural defects caused by particle stacking. On the other hand, the silicone-modified rigid fiber skeleton synergistically improves the water-impact resistance and abrasion resistance of the coating. The crosslinked polysiloxane layer on the SF surface not only provides stable low-surface-energy functional groups to maintain the superhydrophobic state, but also imparts a self-lubricating effect to the coating, which reduces the friction coefficient during reciprocating wear and mitigates material loss. Meanwhile, the rigid cellulose skeleton of SF retained after alkali activation exhibits outstanding mechanical strength and dimensional stability, forming an effective stress transfer and bridging network in the coating. Under the dynamic shear force of water jet impact and the reciprocating normal/shear stress during abrasion, the fibrous network effectively dissipates external stress, inhibits the initiation and propagation of microcracks, and acts as a sacrificial wear phase to protect the micro/nano hierarchical structure constructed by nano-SiO₂ from irreversible damage. Benefiting from the above dual synergistic effects, the composite coating achieves simultaneous improvement in mechanical durability, long-term hydrophobic stability, and structural integrity.

3.3. Long-term superhydrophobic service performance of coatings under extreme environmental damage

Following the evaluation of mechanical robustness, the chemical stability of the superhydrophobic composite coatings under extreme corrosive environments was further assessed via accelerated aging tests in strong acid (HCl, pH = 1) and strong alkali (NaOH, pH = 14) solutions. Using WCA as the core evaluation index, the long-term superhydrophobic service performance of ACR/SiO₂ (20) and ACR/SiO₂(20)-SF (5) coatings was systematically compared, with the corresponding performance degradation mechanism and multi-component synergistic protection mechanism elucidated.

The results of full immersion tests in pH = 1 strong acid solution are presented in Fig. 6a. The WCA of ACR/SiO₂ (20) showed an irreversible and sharp decrease with prolonged immersion time: superhydrophobicity was lost after 8 h (WCA = 143°), and the surface became fully hydrophilic after 48 h with a WCA of only 76°. In sharp contrast, ACR/SiO₂(20)-SF (5) maintained a stable WCA of ~155° throughout the 48 h immersion, with total WCA attenuation below 3% and no obvious superhydrophobicity decay, demonstrating excellent strong acid corrosion resistance.

Full immersion test results in pH = 14 strong alkali solution are shown in Fig. 6b. The performance degradation of ACR/SiO₂ (20) was significantly faster in alkaline medium than in acidic environment: superhydrophobicity was completely lost within 4 h (WCA < 150°), and the surface turned fully hydrophilic after only 24 h with a WCA of 84°. By contrast, ACR/SiO₂(20)-SF (5) retained a stable WCA above 153° during the entire 24 h alkali immersion, with total performance attenuation below 2%, exhibiting exceptional alkaline corrosion resistance.

FE-SEM morphological characterizations (Fig. S1g-j) further validated the distinct difference in structural stability between the two coatings after acid and alkali immersion, which is fully consistent with the aforementioned WCA evolution trends. For the ACR/SiO₂ (20) coating, severe structural collapse and morphological damage were observed after both acid and alkali corrosion. The high loading of hydrophobic fumed silica caused severe particle stacking and agglomeration in the acrylic matrix, generating abundant micro/nano-scale pores and filler-matrix interfacial defects in the as-prepared coating. These inherent defects provide preferential diffusion pathways for aggressive H⁺ and OH⁻ ions, enabling rapid penetration of corrosive media into the coating interior. Specifically, H⁺ ions trigger hydrolytic degradation of the ACR and damage the hydrophobic modification layer of nano-SiO₂, while OH⁻ ions exert a more severe dual corrosive effect: they not only induce saponification of ester groups in the ACR to cause polymer chain degradation, but also directly etch the Si-O-Si backbone of nano-SiO₂, leading to faster structural collapse and hydrophilization of the filler. Ultimately, these effects result in complete destruction of the micro/nano hierarchical structure and irreversible loss of superhydrophobicity.

In contrast, the ACR/SiO₂(20)-SF (5) composite coating retained a dense, intact surface morphology and well-defined micro/nano hierarchical structure after long-term acid and alkali immersion, with no obvious corrosion-induced defects or structural collapse. This excellent corrosion resistance is attributed to the multi-scale synergistic protection effect of SF. On one hand, although the hydrosilylation-grafted polysiloxane layer on the SF surface undergoes slight hydrolysis under strong acid/alkali conditions, the alkali-activated cellulose and lignin skeleton of the fiber itself exhibits excellent intrinsic acid and alkali resistance, maintaining the structural integrity of the fibrous framework in harsh corrosive media. On the other hand, as discussed in the previous sections, the incorporation of SF effectively promotes the uniform dispersion of nano-SiO₂ in the acrylic matrix, eliminating particle stacking-induced pore defects and constructing a highly dense coating structure. The continuous 3D interpenetrating network formed by SF further acts as a physical anti-penetration barrier, significantly retarding the diffusion of aggressive H⁺ and OH⁻ ions, inhibiting resin degradation and filler etching, and thus preserving the structural stability and

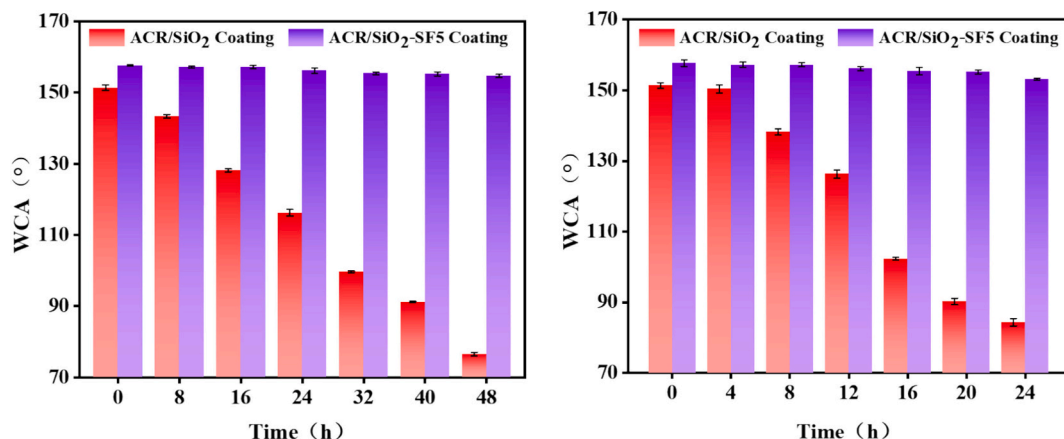


Fig. 6. Evolution of WCA as a function of immersion time for the coatings under harsh corrosive conditions: (a) strong acid environment (pH = 1); (b) strong alkali environment (pH = 14).

superhydrophobic properties of the coating during long-term corrosive service. These findings further confirm the critical role of SF in enhancing the environmental stability of the superhydrophobic composite coatings, which also lays a foundation for its long-term corrosion resistance in simulated marine environments.

Furthermore, the superhydrophobic service durability of the ACR/SiO₂ (20) coating and ACR/SiO₂ (20)-SF (5) composite coating was systematically investigated and compared via accelerated aging tests, including constant thermal oxidation at 120 °C using the WCA as the key evaluation index. The performance degradation mechanisms and long-term protection mechanisms of the coatings under thermo-oxidative were also elucidated.

As shown in Fig. 7, the WCA of the ACR/SiO₂ (20) coating exhibited a continuous linear decrease as the thermal aging time was prolonged from 0d to 7d. After 7d of thermal aging, the WCA dropped to 143°, and the superhydrophobicity was completely lost. The dominant mechanism responsible for this irreversible performance degradation is as follows: when the temperature exceeds the glass transition temperature of the polymer matrix in a high-temperature environment, softening and deformation of the polymeric resin occur, leading to morphological changes of the coating surface. Thermal shrinkage of the resin matrix and agglomeration of fillers irreversibly damage the micro-nano hierarchical rough structure on the coating surface, ultimately resulting in

continuous deterioration of the coating superhydrophobicity. Meanwhile, high temperature induces thermal desorption of the hydrophobic modification groups on the surface of nano-SiO₂, further elevating the surface energy of the coating. In sharp contrast, the ACR/SiO₂ (20)-SF (5) coating maintained a stable WCA of approximately 154° throughout the 7d thermal aging process, retaining superhydrophobicity with a total performance attenuation of less than 2%, demonstrating exceptional thermo-oxidative aging resistance. The outstanding thermal stability originates from the multi-dimensional synergistic protective effect of silicone oil-SF and the long-term retention of the micro-nano hierarchical structure. The three-dimensional network skeleton constructed by silicone oil-SF in the resin matrix exerts a strong anchoring effect on nano-SiO₂ particles, effectively suppressing the agglomeration, migration and detachment of SiO₂ particles at high temperatures. Furthermore, the fibers themselves possess excellent thermal stability, which can permanently preserve the integrity of the micro-nano hierarchical rough structure on the coating surface and ensure that the coating remains stably in the Cassie-Baxter superhydrophobic wetting state.

3.3.1. Analysis of saltwater corrosion resistance of different coatings

The above tests have verified the excellent stability of the ACR/SiO₂ (20)-SF (5) coating under extreme acid, alkali, and high-temperature thermo-oxidative environments. For marine anticorrosion applications, long-term resistance to saltwater immersion is the core evaluation index for practical service performance. Accordingly, the long-term superhydrophobic stability of the coatings was further assessed via full immersion in 3.5 wt% NaCl solution for 90 d, with the WCA evolution results presented in Fig. 8. The WCA of the ACR/SiO₂ (20) coating decreased sharply and continuously with increasing immersion time, reaching only 106° after 90 d and indicating a complete loss of superhydrophobicity. In sharp contrast, the ACR/SiO₂(20)-SF (5) coating maintained a WCA above 150° over the entire immersion period with a total attenuation of less than 2%, demonstrating outstanding long-term saltwater corrosion resistance.

FE-SEM observations further confirmed the distinct structural stability of the two coatings in 3.5 wt% NaCl solution, consistent with the aforementioned WCA evolution (Fig. S3 k,l). After 90 d immersion, the ACR/SiO₂ (20) coating suffered severe collapse of its micro/nano hierarchical structure, extensive SiO₂ detachment, and corrosion-induced microvoids and cracks, resulting in dramatic roughness loss. In contrast, the ACR/SiO₂ (20)-SF (5) coating fully retained its dense, intact hierarchical structure with no obvious corrosion damage.

The irreversible degradation of ACR/SiO₂ (20) arises from aggressive chloride ions (Cl⁻) diffusing through inherent pores and filler-matrix interfacial defects: Cl⁻ damages the hydrophobic modification layer of nano-SiO₂ to cause filler hydrophilization, and induces swelling and

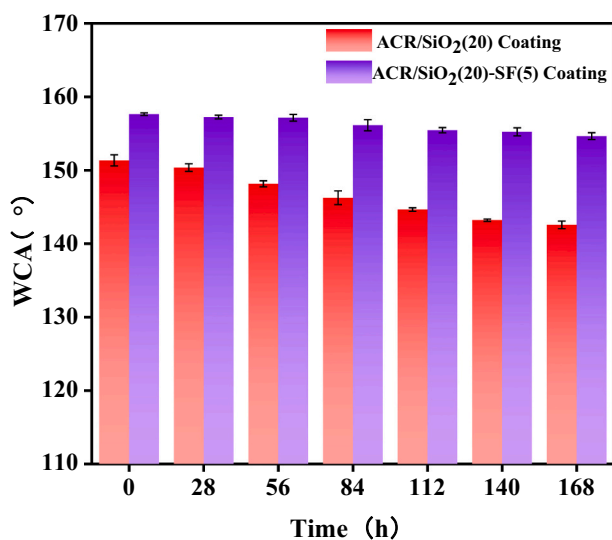


Fig. 7. WCA evolution of superhydrophobic composite coatings during thermal-oxidative aging at 120 °C.

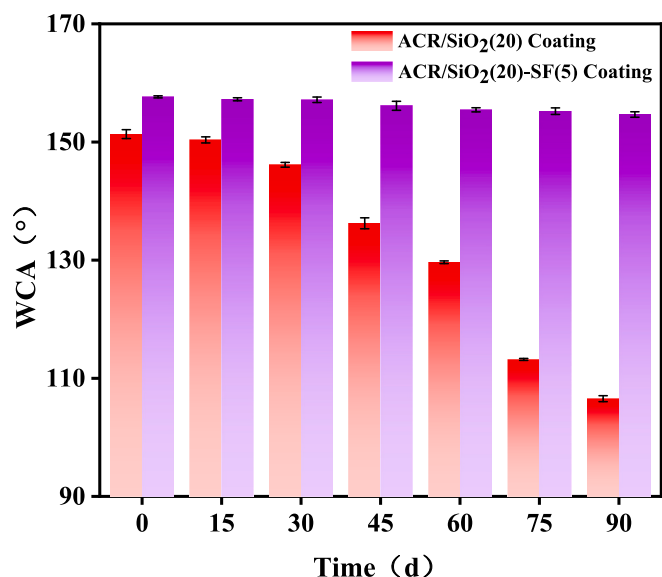


Fig. 8. WCA evolution of superhydrophobic composite coatings during long-term immersion in 3.5 wt% NaCl solution.

hydrolysis of the acrylic matrix to generate hydrophilic groups. These effects destroy the hierarchical roughness and drive an irreversible Cassie–Baxter to Wenzel wetting transition, leading to rapid superhydrophobicity loss. The superior saltwater resistance of ACR/SiO₂

(20)–SF (5) stems from the multi-scale synergistic protection of SF. The 3D fibrous network fills defects to form a dense ion-blocking barrier against Cl[−] and water permeation; the grafted polysiloxane's stable Si–O backbone resists hydrolysis to maintain low surface energy; and strong fiber-matrix adhesion suppresses delamination, preserving the hierarchical structure and stable Cassie–Baxter wetting state.

The above WCA tests and FE-SEM morphological observations have qualitatively revealed the distinct difference in long-term saltwater corrosion resistance between the ACR/SiO₂ (20) and ACR/SiO₂ (20)–SF (5) superhydrophobic composite coatings. EIS, a core non-destructive quantitative characterization technique, was further employed to evaluate the intrinsic protective performance of the coatings, unravel the transport kinetics of corrosive media within the coating matrix, and elucidate the long-term failure mechanism [6,35,36]. In this work, EIS measurements were conducted in a simulated marine corrosive medium (3.5 wt% NaCl aqueous solution) over 0–90 d of full immersion for three coating systems: (1) neat single-layer ACR, Macrynal™ T 5015 coating with a total thickness of 90 μm; (2) double-layer coating consisting of a 60 μm acrylic primer and a 30 μm ACR/SiO₂ (20) topcoat; (3) double-layer coating consisting of a 60 μm acrylic primer and a 30 μm ACR/SiO₂ (20)–SF (5) topcoat. The Nyquist plots, Bode magnitude plots, and Bode phase angle plots were systematically analyzed, with all results presented in Fig. 9.

3.3.2. Nyquist plot analysis

The semicircle diameter in Nyquist plots directly corresponds to the coating impedance modulus, where a larger diameter indicates a stronger insulating barrier against corrosive media (water and Cl[−]), and

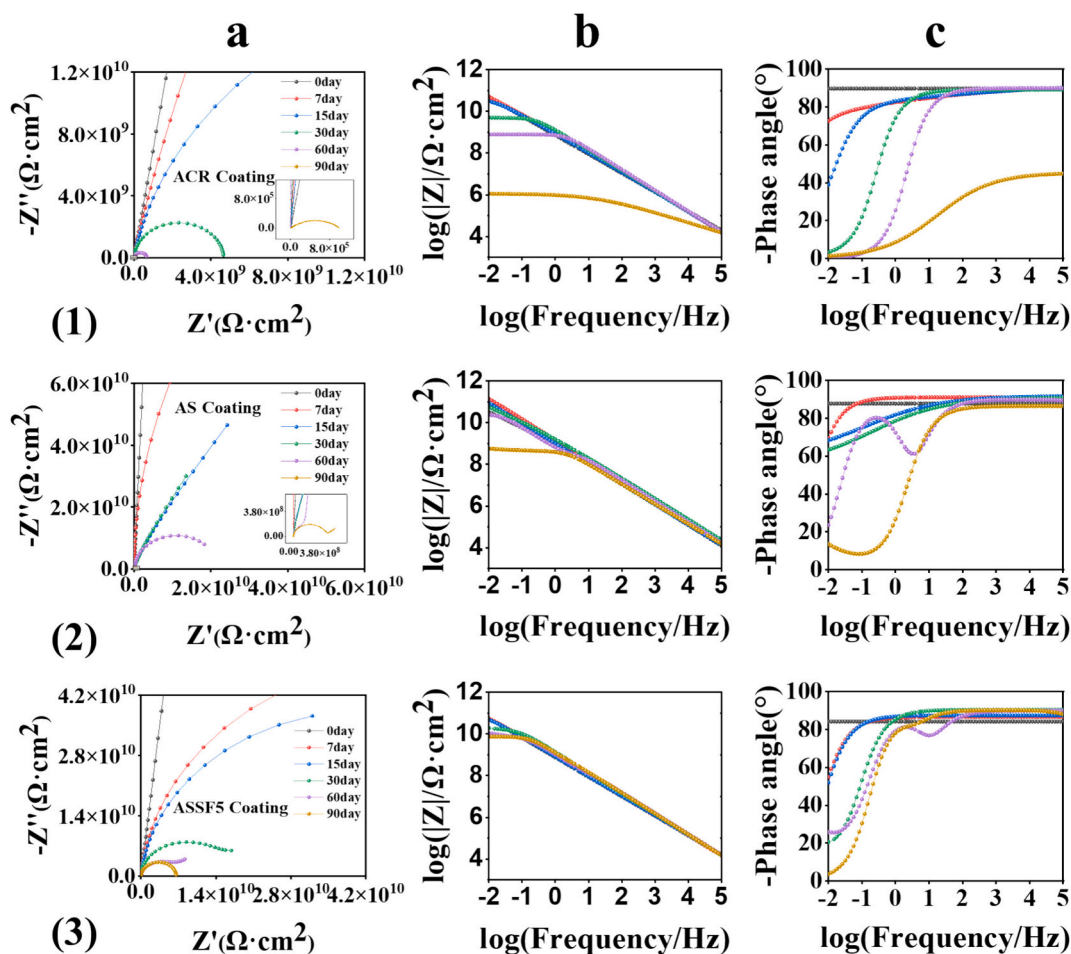


Fig. 9. Electrochemical impedance spectra of different coatings after immersion in 3.5 wt% NaCl solution for 0–90 days: (a) Nyquist plots, (b) Bode modulus plots, (c) Bode phase angle plots; (1) pure ACR coating, (2) ACR/SiO₂ (20) coating, (3) ACR/SiO₂(20)-SF (5) coating.

the semicircle shrinkage rate reflects the decay kinetics of the coating's barrier performance [37,38]. At the initial immersion stage (0 d), all three coatings exhibited a large single capacitive arc with $|Z'| > 10^{10} \Omega \text{cm}^2$ and no high-frequency interfacial response arcs, indicating intact, dense as-prepared films with ideal shielding performance and negligible initial differences.

With prolonged immersion, the capacitive arcs of the three coatings showed distinct evolution trends. The neat ACR coating suffered a continuous, order-of-magnitude decrease in semicircle diameter, falling below $10^{10} \Omega \text{cm}^2$ at 30 d and further to $<10^6 \Omega \text{cm}^2$ at 90 d. The ACR/SiO₂ (20) coating showed a markedly slower impedance decay, maintaining stable performance within 30 d, with obvious semicircle shrinkage only after 60 d and a final diameter of $10^8 \Omega \text{cm}^2$ at 90 d. In sharp contrast, the ACR/SiO₂ (20)-SF (5) coating retained a large, complete single capacitive arc throughout the 90 d immersion with no high-frequency interfacial arcs, demonstrating significantly stronger resistance to media penetration and coating failure than the other two systems.

3.3.3. Bode plot analysis

The Bode magnitude plot reflects the overall impedance of the coating system, where the low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) is the core indicator of long-term protective performance, with a higher value corresponding to stronger corrosion resistance [39,40].

At 0 d, all three coatings achieved an excellent $|Z|_{0.01\text{Hz}}$ of $10^{10} \Omega \text{cm}^2$. With increasing immersion time, the $|Z|_{0.01\text{Hz}}$ of the neat ACR coating decreased continuously and sharply, falling below $10^9 \Omega \text{cm}^2$ at 60 d and to $<10^6 \Omega \text{cm}^2$ at 90 d. The ACR/SiO₂ (20) coating showed a significantly slower decay, maintaining $|Z|_{0.01\text{Hz}}$ above $10^{10} \Omega \text{cm}^2$ at 60 d and declining to $<10^9 \Omega \text{cm}^2$ at 90 d. Notably, the ACR/SiO₂ (20)-SF (5) coating stably retained $|Z|_{0.01\text{Hz}}$ above $10^9 \Omega \text{cm}^2$ throughout the entire 90 d immersion, remaining at an excellent protective level. Its full-frequency curve maintained an ideal slope close to -1 with no low-frequency plateau, indicating pure capacitive behavior and negligible interfacial charge transfer reactions.

3.3.4. Phase angle plot analysis

The height and width of the phase angle peak reflect the capacitive behavior and structural integrity of the coating; a higher and wider phase angle plateau indicates purer capacitive behavior and a more intact, durable barrier [41–43].

At 0 d, all three coatings exhibited a low-frequency phase angle close to 90° with a wide, steep plateau, confirming a dense initial structure and excellent barrier performance. For the neat ACR coating, the phase angle began to decrease slightly at 7 d with medium-high frequency broadening, followed by accelerated decay from 15 to 30 d, a sharp drop in low-frequency phase angle, and plateau shrinkage, indicating media penetration and internal defect formation. After 60 d, the phase angle plateau nearly disappeared, and the low-frequency phase angle plummeted; at 90 d, the maximum phase angle was below 50° , with complete loss of capacitive characteristics, severe interfacial corrosion, and total barrier failure.

The ACR/SiO₂ (20) coating showed a much slower phase angle decay, with only a slight decrease from 7 to 15 d and a retained high low-frequency phase angle and intact plateau at 30 d, confirming that nano-SiO₂ filling prolonged the media penetration path and inhibited early defect propagation. Obvious attenuation and plateau shrinkage occurred after 60 d, but the low-frequency phase angle remained significantly higher than that of the neat ACR coating at 90 d.

In contrast, the ACR/SiO₂ (20)-SF (5) showed negligible phase angle attenuation throughout the immersion period, maintaining a high phase angle and complete plateau with only minimal medium-low frequency broadening. At 90 d, it still retained a high low-frequency phase angle and the widest, steepest plateau with minimal degradation, achieving long-term inhibition of media penetration and interfacial corrosion.

The full-cycle EIS results reveal the essential differences in corrosion failure kinetics and long-term protection mechanisms among the three coating systems at the same total thickness. The neat ACR coating only provides short-term protection, following the classic failure pathway: media wetting and penetration $\rightarrow$ coating swelling $\rightarrow$ through-pore formation $\rightarrow$ media arrival at the metal substrate $\rightarrow$ interfacial corrosion $\rightarrow$ coating delamination and failure. Without superhydrophobic repellency and a gradient protection structure, corrosive media rapidly penetrate through inherent curing defects, leading to significant failure after 60 d of immersion.

The ACR/SiO₂ (20) double-layer coating constructs a gradient protection system: the nano-SiO₂-built micro/nano hierarchical structure endows superhydrophobicity to suppress electrolyte wetting and capillary penetration at the source, while nano-SiO₂ filling in the topcoat extends the media penetration path, delaying infiltration from the topcoat to the primer and thus improving anticorrosion durability.

The long-term anticorrosion mechanism of the ACR/SiO₂(20)-SF (5) composite coating is illustrated in Fig. 10, centered on a triple synergistic protection system: surface superhydrophobic repellency, internal physical barrier, and long-term structural stability.

- 1. Surface barrier:** The micro–nano hierarchical rough structure synergistically constructed by SF and hydrophobic nano-SiO₂ stably traps air to form a continuous air isolation layer, conforming to the Cassie–Baxter superhydrophobic wetting model. This fundamentally inhibits surface wetting and capillary penetration of corrosive media (H₂O, Cl[−]), greatly reducing media intake as the first defensive barrier.
- 2. Internal barrier:** The one-dimensional rod-like SF forms an interlaced continuous three-dimensional network skeleton in the ACR matrix, complementing uniformly dispersed nano-SiO₂ particles. This effectively fills inherent pores and filler–matrix interfacial defects, reduces overall coating porosity, and constructs a labyrinthine diffusion barrier that drastically prolongs the transport path of corrosive media. It dynamically slows the penetration rate of H₂O and Cl[−] and blocks diffusion channels to the metal substrate, serving as the second core physical barrier.
- 3. Structural stability:** The high-bond-energy, chemically inert polysiloxane layer grafted on SF, excellent media resistance of the fiber itself, and good interfacial compatibility with the ACR matrix jointly preserve the integrity of the protective structure during long-term immersion, avoiding premature coating–substrate debonding and barrier failure.

To rigorously evaluate the durability of the optimized ACR/SiO₂(20)-SF (5) coating, a systematic comparative analysis was performed against state-of-the-art superhydrophobic coating systems reported in existing literature, with key performance metrics summarized in Table S1. All comparative assessments were conducted in strict compliance with the ISO/TS 10689 protocol to ensure the validity and reliability of cross-system benchmarking.

As presented in Table S1, the ACR/SiO₂(20)-SF (5) coating exhibits prominent advantages in both long-term corrosion resistance and green sustainability. Specifically, the coating delivers exceptional long-term saltwater corrosion tolerance: after 90 days of continuous immersion in 3.5 wt% NaCl solution, its water contact angle (WCA) remains above 150° , maintaining a stable superhydrophobic state. This service duration is over 12 times longer than that of the best-performing silicone-resin-based reference system (7 days), and far exceeds the tolerance limit of 1–7 h for epoxy-based and polyester-based coatings under identical saline conditions. The labyrinthine physical barrier structure constructed by silicone-modified corn straw fibers effectively retards the penetration of corrosive chloride ions, endowing the coating with outstanding long-term protection for carbon steel in high-salinity marine environments. Furthermore, the as-developed coating also outperforms most reported systems in long-

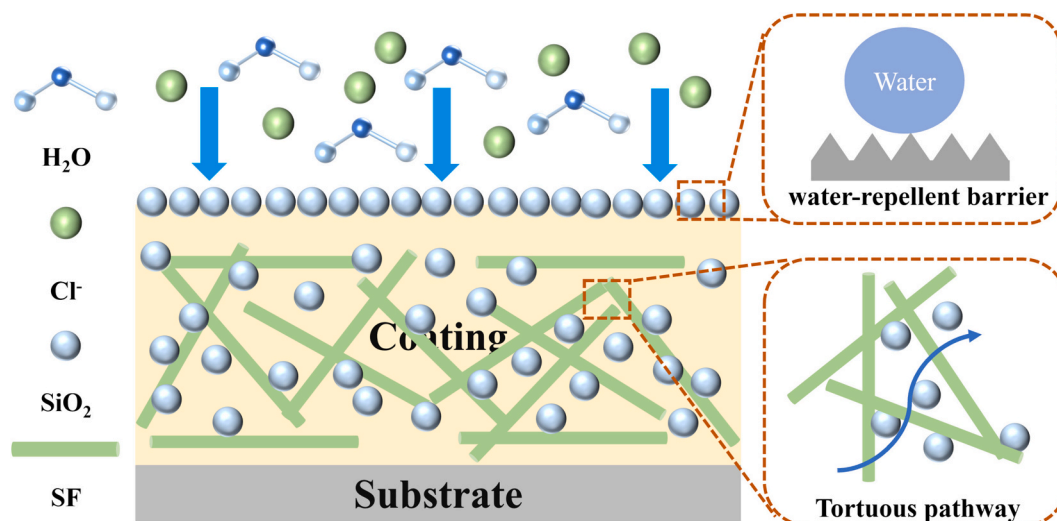


Fig. 10. Schematic diagram of the anticorrosion mechanism of ACR/SiO₂(20)-SF (5) composite coating.

term acid and alkali resistance. After 48 h of immersion in HCl solution (pH = 1) and 24 h of immersion in NaOH solution (pH = 14), the coating retains favorable superhydrophobic stability. In contrast, most epoxy-based coatings can only withstand 1–12 h of strong acid/alkali immersion, and even the silicone-resin-based coating with the optimal alkali resistance merely achieves a maximum tolerance duration of 16 h at pH = 14. Additionally, distinct from most reported superhydrophobic coatings that rely on fluorinated components such as polytetrafluoroethylene (PTFE) and perfluoroalkyl substances to reduce surface energy, this work adopts agricultural waste corn straw fibers and hydrophobic SiO₂ as functional fillers, where the corn straw fibers are hydrophobically modified solely via silicone treatment. This fluorine-free formulation eliminates the environmental accumulation risk associated with fluorine-containing substances, while simultaneously realizing high-value utilization of biomass resources.

The above comparative results confirm that the synergistic combination of acrylic resin matrix, hydrophobic SiO₂ and SF provides a green and high-performance strategy for long-term corrosion protection of carbon steel, effectively reconciling the long-standing trade-off between green sustainability and durable protective performance in conventional superhydrophobic coatings.

4. Conclusions

A green, cost-effective and robust superhydrophobic composite coating (ACR/SiO₂-SF) was successfully fabricated using agricultural waste corn straw as the raw material; CFs were subjected to alkali activation and hydrosilylation modification to obtain silicone oil-functionalized fibers (SF), which were further synergistically incorporated with hydrophobic nano-SiO₂ into an ACR matrix. Results indicate that the ACR/SiO₂(20)-SF (5) coating achieves the optimal overall performance, presenting a WCA of 158.14° and a SA of 2°, with stable superhydrophobicity, self-cleaning ability and multi-liquid non-wettability. Benefiting from the three-dimensional network bridging effect and improved interfacial compatibility imparted by SF, the composite coating reaches Grade 0 cross-cut adhesion and exhibits outstanding mechanical durability against sandpaper abrasion and water jet impact, while maintaining excellent stability under extreme environments including strong acid, strong alkali, high-temperature oxidation, and long-term saltwater immersion with performance attenuation below 3%. Long-term electrochemical measurements over 90 d in 3.5 wt% NaCl solution confirm that the ACR/SiO₂(20)-SF (5) coating retains a high low-frequency impedance modulus above 10⁹ Ωcm², revealing superior long-term corrosion resistance, and the protective mechanism

arises from a triple synergistic effect: the surface superhydrophobic air layer repels corrosive media penetration, the internal fiber-SiO₂ interpenetrating network constructs a tortuous diffusion barrier to retard ion transport, and the stable polysiloxane layer preserves structural integrity during prolonged service. This work realizes high-value utilization of agricultural waste corn straw and addresses the critical limitations of conventional superhydrophobic coatings including poor adhesion, insufficient durability and short service life; the as-developed green, low-cost and high-performance coating provides a promising strategy for long-term corrosion protection of metallic components in harsh marine and chemical environments, and offers theoretical and technical support for the scalable application of biomass fibers in functional anticorrosive coatings.

CRediT authorship contribution statement

Congcong Zhang: Writing – original draft, Methodology, Conceptualization. **Haohan Huang:** Investigation, Formal analysis. **Xinyu Wang:** Validation, Resources. **Wei Lu:** Supervision, Resources. **Qiang Lei:** Visualization, Data curation. **Rulin Li:** Formal analysis. **Yilin Jiang:** Validation, Data curation. **Xiao Wang:** Resources, Software. **Yan Sun:** Validation, Software. **Weili Li:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2026.110459>.

Data availability

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

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