



Silicone-modified acrylic hybrid latex: film formation and performance

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Abstract Traditional waterborne acrylic latex formulations commonly rely on substantial quantities of hydrophilic monomers and additives during synthesis, which often result in coatings exhibiting high surface hydrophilicity. This inherent hydrophilicity adversely affects key performance attributes such as antifouling and corrosion resistance in the cured films. To address these limitations, an organosilicone-modified acrylic latex was successfully synthesized via in-situ emulsion polymerization. A key innovation of this work involves

the development of a effective strategy to overcome interfacial compatibility issues between polymer phases with significantly different polarities. This was achieved through the establishment of chemical bonds between the organosilicone and acrylic resins, allowing their encapsulation by surfactant micelles and enabling homogeneous dispersion within the aqueous phase. Structural and morphological analyses including Fourier transform infrared spectroscopy, dynamic light scattering for particle size and zeta potential measurements, and transmission electron microscopy—confirmed that the hybrid latex particles adopted a core-shell-like architecture encapsulated by surfactant micelles, thereby promoting colloidal stability in water. During film formation, water evaporation induced capillary forces that drove particle approximation, deformation, and coalescence, ultimately leading to emulsion destabilization. The hybrid latex exhibited self-stratification behavior attributable to differences in polarity and density between the constituent polymers, as evidenced by field-emission scanning electron microscopy (FE-SEM). This resulted in the migration of organosilicone components toward the coating–air interface, imparting the final films with enhanced heat resistance, antifouling characteristics, surface hydrophobicity, and improved corrosion resistance. These findings underscore the effectiveness of the in-situ modification approach in improving the functional properties of waterborne acrylic coatings via controlled phase separation and surface enrichment with organosilicone constituents.

Ruofei Liu and Xiao Wang have contributed equally to this work.

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Introduction

Acrylic latex, a prominent class of polymer dispersions, has garnered substantial attention in the coatings industry due to its favorable material properties.¹ These water-based systems are highly regarded for their excellent color retention, environmental compatibility, and resistance to acids and alkalis, making them a preferred binder for metal corrosion protection.^{2–4} However, when used in anti-corrosion applications, conventional acrylic latexes exhibit several inherent limitations that can compromise their protective performance.^{5–7} A major drawback is their inherent permeability to water and corrosive agents.⁸ The high concentration of hydrophilic carboxyl groups and residual emulsifiers within the latex facilitates the formation of continuous hydrophilic pathways, enabling the penetration of moisture and aggressive species. This compromises the coating's barrier properties and long-term durability.^{9,10} Moreover, the emulsion polymerization process often introduces structural defects—both macro and micro—that can act as channels for corrosion initiation and propagation.^{11–13} Furthermore, the high polarity and surface tension of waterborne acrylic emulsions can lead to inadequate adhesion and poor wet scrub resistance on non-absorbent substrates, restricting their use in certain high-performance coating applications.¹⁴

The enhancement of the anti-corrosion performance of waterborne acrylic latex-based coatings can be approached from several perspectives. Firstly, the introduction of functional groups into the polymer resin can improve coating properties. For instance, polar groups such as hydroxyl and carboxyl groups can significantly enhance adhesion strength.^{15–17} Secondly, the adoption of a core-shell structured latex offers a promising strategy. In such systems, the core component contributes to film formation and flexibility, while the shell can improve hardness, water resistance, and other key properties.^{18,19} Thirdly, crosslinking modification can be employed to form a three-dimensional network within the coating, thereby increasing its compactness and overall performance.^{20,21} Fourthly, the incorporation of flake-shaped pigments and fillers can extend the penetration path of corrosive media, while active anti-corrosion pigments can facilitate the formation of a passive protective layer on the substrate surface.²² Furthermore, it is essential to optimize application parameters and control environmental conditions such as temperature and humidity during the coating process.

Furthermore, the properties of acrylic resin can also be optimized and modified by employing polymeric resins containing functional groups, such as epoxy or organosilicon groups. Such resins can be incorporated into acrylic resins through blending to impart novel functionalities to the cured coatings. A notable example is organosilicone resins, which are widely recognized for their multifunctional advantages in coating appli-

cations.²³ These resins possess exceptional heat resistance, enabling sustained performance at elevated temperatures; excellent weatherability, which provides resistance to ultraviolet degradation; and superior electrical insulation properties, making them suitable for use in electronic and electrical devices.^{24–26} Additionally, they are characterized by high chemical stability, low surface energy, and favorable release properties. Consequently, organosilicone-modified acrylic resins present a promising strategy for developing advanced functional coatings with enhanced performance.²⁷

Zhao et al. developed a self-healing liquid/liquid-like polymer brush hybrid coating by constructing an amphiphilic polydimethylsiloxane (PDMS)-based polysiloxane sol. This system emulsifies free silicone oil into nanoscale silicone oil pools that function as a lubricant reservoir, enabling autonomous self-repair without external energy input.²⁸ Canosa et al.²⁹ synthesized a high-solids coating using a diglycidyl ether of 1,4-butanediol aliphatic epoxy resin cured with amino-propyl methyldiethoxysilane and chemically modified with alkoxysilane. The resulting hybrid coating exhibited enhanced corrosion resistance but reduced blistering resistance, attributed to improved alkoxide reactivity and stronger chemical interactions with the substrate.

Gedan-Smolka et al.³⁰ reported a melt-processable self-stratifying coating based on silicone/epoxy blends, fabricated via an eco-friendly, industrially scalable, and user-friendly process. Peng et al.³¹ proposed an organic/silicone hybrid coating system using amine-terminated hyperbranched polysiloxane (SHPSi) as a latent curing agent and a diisocyanate containing a small amount of perfluoropolyether (PFPE) as an organic linker. Upon exposure to moisture, the mixture cures at room temperature, forming a smooth, low-surface-energy coating with high transparency (transmittance > 90%) and outstanding antifouling properties. The coating also demonstrated high stability against various corrosive solutions and UV radiation. Notably, it is applicable to diverse substrates and suitable for large-area applications.

Our research group has previously conducted relevant studies in this area.^{32,33} A distinctive feature of our work lies in the establishment of chemical bonding between acrylic and silicone resins, effectively addressing the long-standing challenge of poor compatibility between these two phases in physically blended systems. The resulting hybrid resins exhibit self-stratification behavior during the curing process, endowing the cured coatings with enhanced hydrophobicity, improved heat resistance, and superior corrosion protection. These properties make the materials highly promising for anti-smudge applications. However, it should be noted that the current system relies on the volatilization of non-environmentally friendly solvents, which may pose potential environmental hazards.

In this study, a hybrid latex was synthesized via emulsion polymerization using deionized water as the

solvent, in which functional silicone resins and acrylic monomers were encapsulated within emulsifier micelles and uniformly dispersed in the aqueous phase. A systematic investigation was carried out to examine: (i) the effective compounding mechanism between the two polymer phases; (ii) the formation of self-stratifying structures during film formation; and (iii) the influence of the resulting coating morphology on the properties of the cured films.

Experimental section

Materials

Divinylbenzene (DVB, A.R.) was provided by Jiangsu Wuxi Jiasheng Pharmaceutical Chemical Equipment Co., Ltd. Styrene (St, C.P.), isooctyl acrylate (2-EHA, C.P.), methacrylic acid (MAA, C.P.), and hydroxyethyl acrylate (HEA, C.P.) were obtained from Jiangsu Qiangsheng Functional Chemical Co., Ltd. Poly-methylhydrosiloxane (PHMS, hydrogen content: 0.1%) was purchased from Shanghai Xibao New Material Co., Ltd. Platinum catalyst (A.C.) was supplied by Shenzhen Ke Junqi Technology Co., Ltd. Ammonium persulfate (APS, A.R.) was obtained from China Pharmaceutical Group Chemical Reagent Co., Ltd. Anionic emulsifier (ABEX DBR-Z, Solvay), nonionic emulsifier (MARLOX RT 64, Sasol), coalescing agent (Texanol, Eastman), and flash rust inhibitor (ASCOTRAN-H10, ASCOTEC®) were purchased from commercial sources. All chemicals were used as received without further purification.

Synthesis of the AL-PHMS-X hybrid latex

In this study, divinylbenzene-modified polyhydromethylsiloxane (D-PHMS), synthesized according to a previously reported method,³² was employed as a reactive modifier for acrylic latex. D-PHMS was first blended with acrylate monomers—including styrene (St), hydroxyethyl acrylate (HEA), and methacrylic acid (MAA)—and subsequently incorporated into the latex via semi-continuous emulsion polymerization, resulting in a hybrid latex capable of self-stratification.

To systematically evaluate the effect of D-PHMS content on the properties of the hybrid latex, the glass transition temperature (T_g) of the acrylic base was fixed at 15 °C, while the relative content of D-PHMS was varied from 2 to 8 wt%. A schematic illustration of the synthesis process is provided in Fig. 1, with additional experimental details available in the Supporting Information. For clarity, the resulting hybrid latexes are designated as AL-PHMS-X, where X corresponds to the weight percentage of D-PHMS (ranging from 2 to 8 wt%).

Preparation of the coatings based on AL-PHMS-X

To investigate the self-stratification behavior of the AL-PHMS-X coatings and correlate their morphologies with the final properties, both steel panels and silica glass slides were employed as substrates. The steel substrates were first abraded with sandpaper and subsequently degreased with ethanol to ensure a clean, dust-free surface. Prior to application, the AL-PHMS-X formulations were mixed with appropriate amounts of coalescing agent and flash rust inhibitor. The resulting mixtures were then applied using a wire-wound bar coater. Coatings were cured at room temperature for 24 h, with dry film thicknesses maintained at 90 µm for steel and 60 µm for glass substrates, respectively.

Characterizations

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS50 spectrometer (Thermo Fisher Scientific, USA). The morphology of AL-PHMS-X latex particles in aqueous dispersion was examined by transmission electron microscopy (TEM, Tecnai G220, FEI Company) operated at an accelerating voltage of 200 kV. Surface and cross-sectional morphologies of the cured coatings were characterized using a JSM-6480 scanning electron microscope (SEM, Shimadzu, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS) for elemental analysis and mapping. The glass transition temperature (T_g) of the AL-PHMS-X latex was determined using a Diamond DSC8000 differential scanning calorimeter (PerkinElmer Instruments Co., LTD., USA). Zeta potential and particle size measurements were conducted at room temperature with a 90Plus Zeta Potential and Particle Size Analyzer (Brookhaven Instruments, USA). Mechanical properties of the coatings were evaluated using standardized methods. Toughness was assessed via a QTY-32 film bending tester (State-owned Tianjin Weida Testing Machine Factory) in accordance with GB/T 1731-2020. Impact resistance was tested with a BGD 302 tubular impact tester following GB/T 20624.2-2006. Coating hardness was measured using the pencil hardness method per GB/T 6739-2006, and adhesion strength was determined with a BGD500 digital adhesion tester (Sanfeng Precision Measuring Instrument Guangdong Co., LTD.) according to GB/T 5210-2006. Surface wettability was characterized by contact angle measurements using a Theta Lite instrument (Biolin Scientific, Germany) with distilled water as the probe liquid ($\gamma = 72.8$ mN/m; $\gamma_d = 21.8$ mN/m; $\gamma_p = 51$ mN/m). The corrosion resistance of the coatings was evaluated electrochemically using a CHI660A workstation. Tafel polarization and electrochemical impedance spectroscopy (EIS) measurements were carried out in a 3.5 wt% NaCl solution, employing the coated steel as the working electrode, a platinum counter electrode, and a saturated calomel electrode

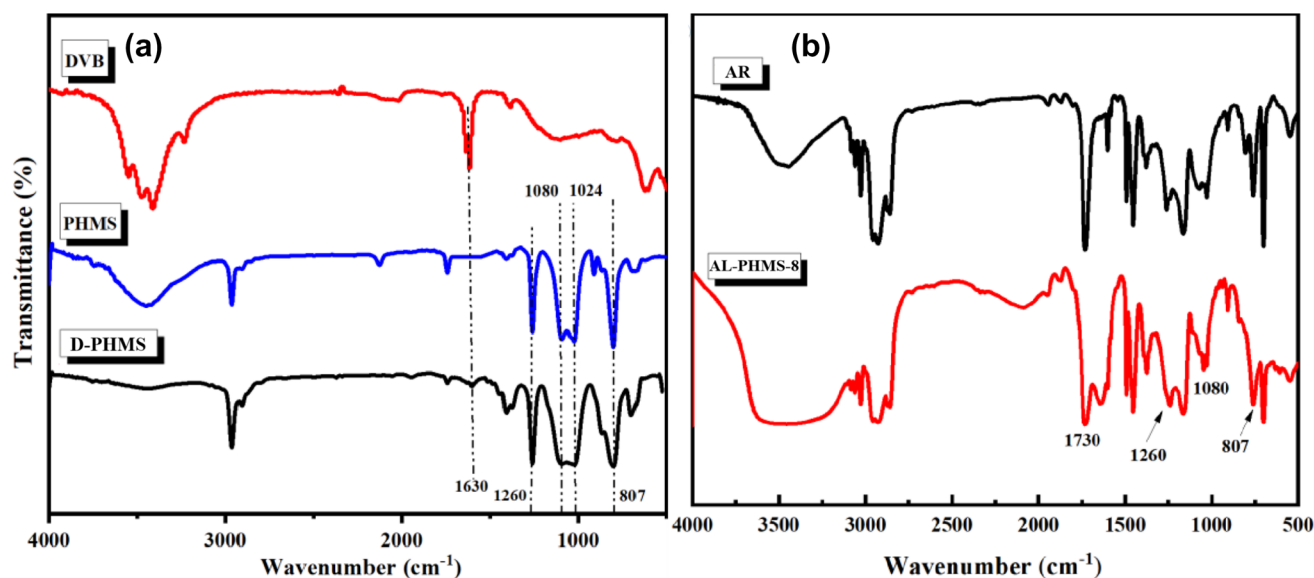


Fig. 1: Comparison of the FTIR spectra of (a) DVB, PHMS, and D-PHMS; (b) Ordinary acrylic latex and AL-PHMS-8

(SCE) as the reference. The exposed coating area was 9.6 cm^2 .

Results and discussion

The chemical composition and morphology analysis of the AL-PHMS-X

Owing to the presence of reactive Si-H groups, PHMS resin can function as an electrophilic reagent and undergo electrophilic addition with electron-rich organic compounds. The reaction products were verified by FTIR spectroscopy. As shown in Fig. 1(a), the spectrum of D-PHMS displays strong broad absorption bands near 1080 cm^{-1} and 1024 cm^{-1} , which are assigned to the bending vibrations of Si-O-Si bonds. Peaks observed at 1260 cm^{-1} and 806 cm^{-1} are attributed to the bending vibrations of C-Si-C bonds. Notably, the characteristic peak at 2125 cm^{-1} originating from the stretching vibration of Si-H in pure PHMS is significantly diminished and nearly absent in D-PHMS, confirming the effective consumption of Si-H groups and successful chemical bonding between PHMS and DVB. Furthermore, the appearance of an absorption peak at 1630 cm^{-1} in D-PHMS corresponds to the C=C functional group, enabling subsequent participation in radical polymerization with acrylate monomers. Figure 1(b) compares the FTIR spectra of conventional acrylic latex and the AL-PHMS-8 hybrid. Peaks at 1730 cm^{-1} and 1600 cm^{-1} are associated with the C=O stretching vibration of the carbonyl group and the skeletal vibration of the benzene ring, respectively. Additionally, the presence of absorption bands at 806 cm^{-1} , 1024 cm^{-1} , and 1260 cm^{-1} —characteristic of the PHMS component—confirms the successful incorpo-

ration of D-PHMS into the acrylic polymer matrix via emulsion polymerization. These results collectively verify the effective synthesis of the AL-PHMS-8 hybrid latex.

The particle size, size distribution, and zeta potential of latex particles play critical roles in determining the viscosity and storage stability of the emulsion.³⁴ Furthermore, these parameters considerably influence key properties of the resulting coatings, such as water resistance, transparency, and surface gloss. To examine the effect of D-PHMS copolymerization on the characteristics of the latex particles, zeta potential measurements were conducted using a 90Plus Zeta analyzer, and morphological observations were carried out by transmission electron microscopy (TEM).

Table 1 summarizes the particle size and zeta potential values of the various hybrid latexes, with detailed distributions provided in Fig. S1. The results indicate that all samples exhibit nanoscale particle sizes. As the D-PHMS content increases, the particle size initially decreases and then increases, while the zeta potential follows an inverse trend. Compared to conventional acrylate monomers, D-PHMS possesses lower polarity. During emulsion polymerization, D-

Table 1: The particle size and zeta potential of the different hybrid latexes

Sample	Diameter (nm)	Zeta potential (mV)
AR	79.336	− 35.22
AL-PHMS-2	70.845	− 41.25
AL-PHMS-4	60.171	− 52.16
AL-PHMS-6	59.254	− 56.21
AL-PHMS-8	64.198	− 47.05

PHMS tends to migrate into the hydrophobic cores of the surfactant micelles. At lower concentrations, the micelles effectively encapsulate the hydrophobic D-PHMS, promoting the formation of a stable hybrid latex structure with a hydrophobic interior and hydrophilic shell. This configuration contributes to a reduction in particle size and an increase in zeta potential. However, D-PHMS is an oligomer with a substantial molecular weight ($M_n = 6000\text{--}8000$ g/mol). When incorporated in excessive amounts, the encapsulation capacity of the micelles is exceeded, compromising the structural integrity of the latex particles. This leads to aggregation, an increase in particle size, and a corresponding decline in zeta potential (Table 2).

Figure 2(a) and (b) present TEM images of AL-PHMS-6 and AL-PHMS-8, respectively. At lower D-PHMS content, the latex particles exhibit a well-defined spherical morphology with compact structure, indicating effective encapsulation of the hydrophobic D-PHMS within the polymer particles. In contrast, when an excessive amount of D-PHMS was incorporated, the surfactant micelles were unable to fully accommodate the oligomeric silicone component, resulting in irregularly shaped particles with loose morphology and compromised colloidal stability.

These findings collectively demonstrate that, when introduced in appropriate quantities, D-PHMS can be effectively copolymerized with acrylate monomers via emulsion polymerization to form a stable hybrid latex system.

The influence of D-PHMS component on morphology the cured coatings based on the AL-PHMS-X

To investigate the morphology of the cured coating and evaluate the formation of a self-stratified structure, AL-PHMS-6 was selected as a representative sample. Its surface and cross-sectional morphologies were examined using scanning electron microscopy (SEM).

Figure 3(a) presents the surface morphology of the cured AL-PHMS-6 coating, which appears homogeneous and free of defects such as shrinkage cavities. This suggests that the film-forming agent effectively facilitates the coalescence of the hybrid latex particles via capillary-driven rearrangement during drying, leading to the formation of a continuous and uniform film.

Figure 3(b) shows the cross-sectional morphology of the coating, which exhibits a clear bilayer fracture structure. The upper layer displays a ductile fracture mode with fibrillar features and microcracks, while the lower layer is characterized by a smooth, brittle fracture surface. This structural differentiation is attributed to the incorporation of D-PHMS. During film formation, the dissociation of micelles releases polymer chains with differing polarities and densities. Due to its lower density ($0.93\text{--}0.96$ g/cm³) compared to the acrylic resin (1.14 g/cm³), the D-PHMS component migrates preferentially toward the air interface.³⁵ Covalent bonding between D-PHMS and the acrylate segments, however, suppresses macroscopic phase separation, resulting in a self-stratified structure with a continuous compositional gradient. Energy-dispersive X-ray spectroscopy (EDS) mapping confirmed the enrichment of silicon in the upper layer, with the Si/O atomic ratio increasing by 23% compared to the lower region. The enhanced elasticity of the top layer can be ascribed to the flexibility of the Si–O–Si bonds, which exhibit a longer bond length (1.64 Å vs. 1.53 Å for C–C) and a wider bond angle (143° vs. 110°). This molecular structure imparts improved mechanical resilience to the coating, allowing plastic deformation under stress and resulting in the observed ductile fracture behavior in the upper section.

The influence of D-PHMS component on properties of the cured coatings based on the AL-PHMS-X

The thermophysical properties of the coatings

To evaluate the influence of copolymerized PHMS on the thermodynamic properties of the hybrid latex, differential scanning calorimetry (DSC) was performed on systems with varying D-PHMS contents (Fig. 4a). The theoretical glass transition temperature (T_g) of the pure acrylic latex, calculated using the Fox equation, was 15°C , which is consistent with the experimentally determined T_g of 17.6°C obtained via DSC. A clear trend was observed: the T_g of the cured coatings increased systematically with rising D-PHMS content. Although pure PHMS possesses flexible polymer chains, its modification with divinylbenzene introduces multiple functional reactive sites. These groups promote the development of a crosslinked network during

Table 2: The mechanical properties of the dried AL-PHMS-X coatings

Sample	Flexibility (mm)	Pencil hardness	Impact resistance (kg·cm)	Adhesion property (MPa)
AR	1	B	40	1.32
AL-PHMS-2	0.5	HB	45	1.28
AL-PHMS-4	0.5	HB	50	1.23
AL-PHMS-6	0.5	H	50	1.11
AL-PHMS-8	0.5	H	50	1.03

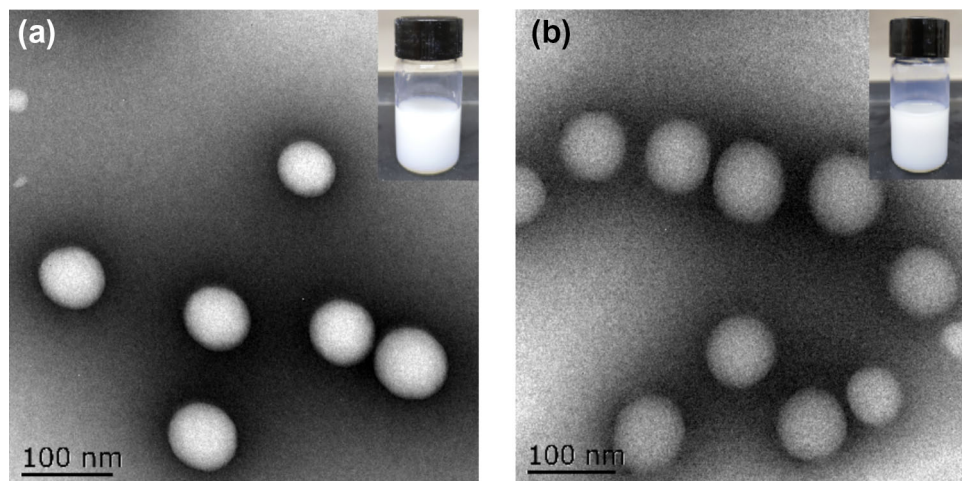


Fig. 2: TEM morphologies of the different hybrid latexes a AL-PHMS-6; b AL-PHMS-8

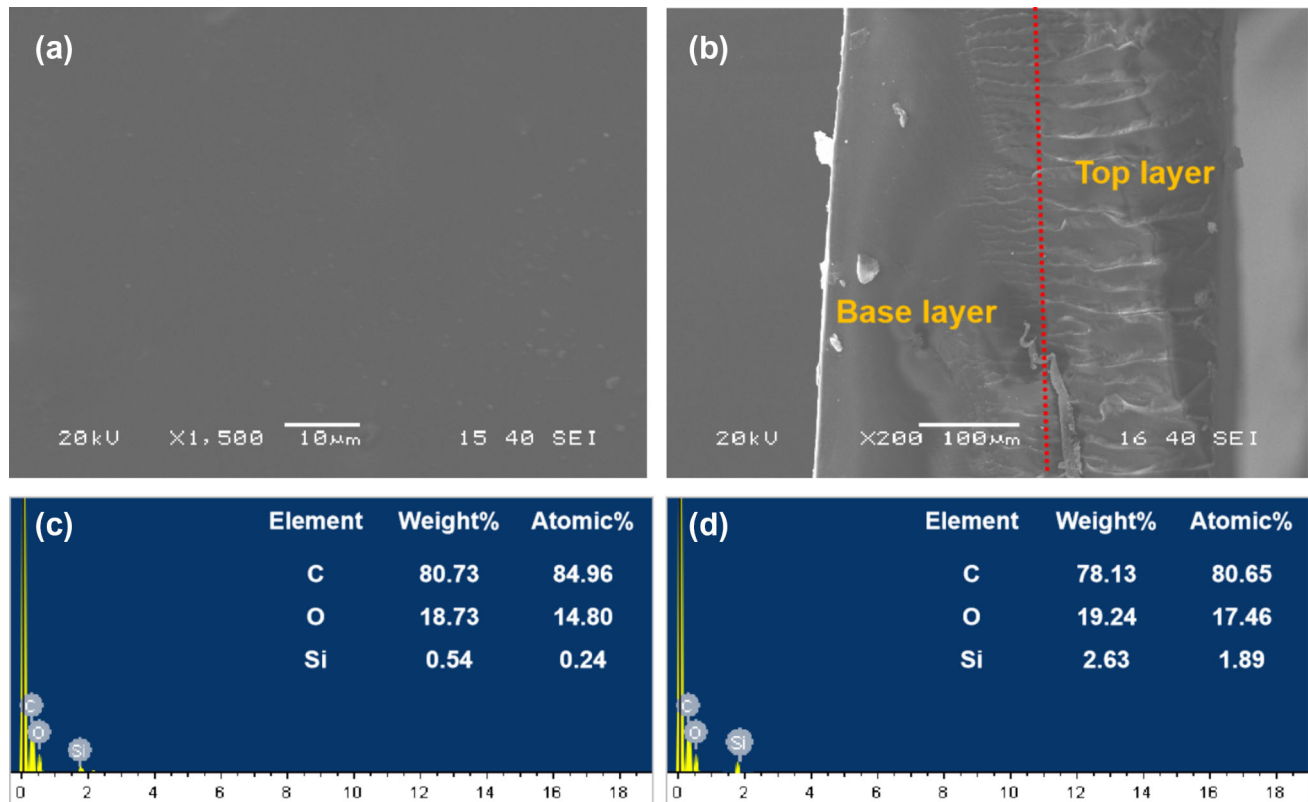


Fig. 3: SEM images of AL-PHMS-6 (a) the surface morphology; and (b) cross-sectional morphology; EDS analysis of the AL-PHMS-6 (c) the bottom layer and (d) the top layer

copolymerization with acrylate monomers, which restricts segmental motion of the polymer chains and leads to the observed increase in T_g in the cured hybrid systems.³⁶

To further investigate the effect of D-PHMS content on the thermal stability of the cured coatings, thermogravimetric analysis (TGA) was conducted (Fig. 4b). The decomposition temperatures corresponding to 10% and 50% mass loss, along with the residual char

yields, are summarized in Table S2. Initial mass loss observed near 102 °C across all samples is attributed primarily to the evaporation of residual moisture. A significant decrease in weight commenced around 351 °C, marking the onset of the main thermal degradation stage. Notably, at any given temperature, the pure acrylic resin exhibited substantially greater mass loss compared to the D-PHMS-modified hybrid latexes. Moreover, the thermal stability of the hybrid coatings

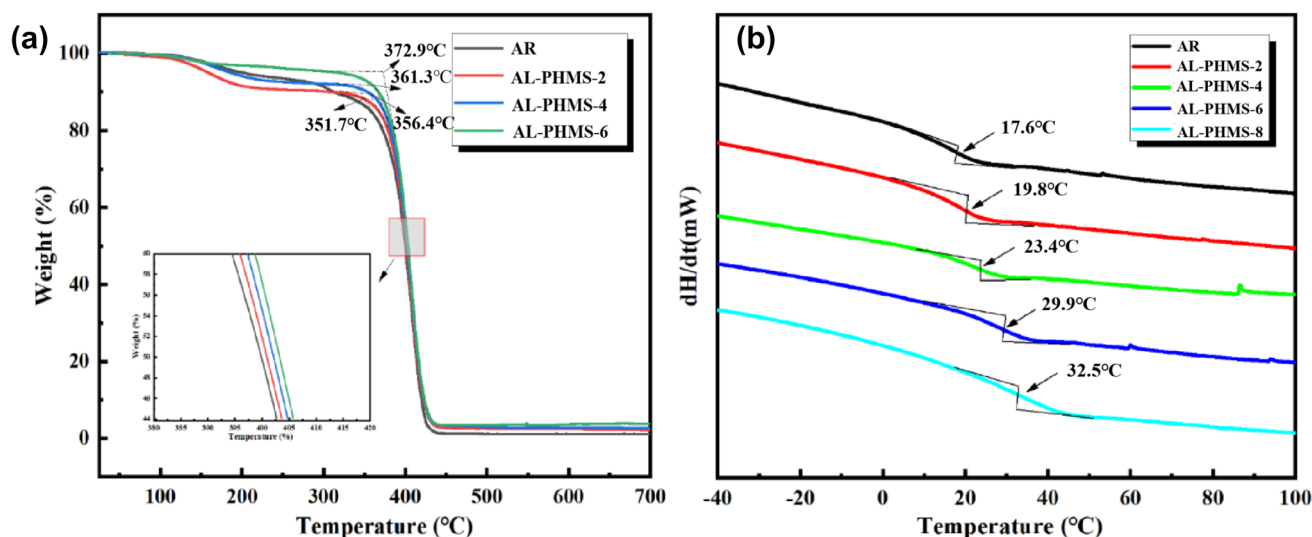


Fig. 4: (a) DSC curves and (b) TGA analysis of the cured AL-PHMS-X with different D-PHMS content

improved with increasing D-PHMS content, as evidenced by reduced mass loss rates and higher residual masses. This enhancement can be ascribed to two key factors: firstly, the higher bond dissociation energy of Si–O (450 kJ/mol) compared to C–C (332 kJ/mol) and C–O (326 kJ/mol) imparts greater inherent thermal stability to the polysiloxane segments. Secondly, the crosslinked network formed by D-PHMS restricts chain mobility and retards thermal degradation. Above 440 °C, the modified coatings showed increased char residue, consistent with the formation of thermally stable silica-like structures. Throughout the temperature range studied, the silicone-rich domains demonstrated superior stability without noticeable decomposition.

The mechanical properties of the cured coatings

Mechanical properties are critical indicators for evaluating the performance of coatings in practical applications. Enhancing key parameters such as hardness, flexibility, adhesion, and impact resistance can significantly improve the protective functionality of coatings, thereby extending the service life of the underlying substrate. A thorough understanding and systematic optimization of these mechanical properties are essential to ensure high performance and durability in coating applications.⁵⁷ Such efforts not only contribute to reliable substrate protection but also facilitate technological innovation across various industries. The hardness of the coating was observed to increase with higher D-PHMS content. As previously discussed, the glass transition temperature (T_g) of the AL-PHMS-X coatings rises linearly with increasing D-PHMS incorporation, which can be attributed to the elevated crosslinking density within the coating matrix. In contrast, the adhesion of the

cured coatings showed a slight reduction. Although the AL-PHMS-X coating forms a self-stratified structure, a small fraction of organosilicon segments remains near the substrate interface. The low cohesive energy density and weak intermolecular forces characteristic of silicone resins contribute to this moderate decline in adhesion. Nevertheless, the adhesion strength of all formulated coatings remained above 1 MPa. Notably, all AL-PHMS-X coatings exhibited excellent flexibility and impact resistance. From a molecular perspective, the high flexibility of the silicone components originates from the free rotation of Si–O bonds in the siloxane backbone and the low steric hindrance among methyl groups. This molecular mobility ensures outstanding compliance under both static (flexibility) and dynamic (impact resistance) mechanical conditions.

The surface tension performance of the cured coatings

Owing to the self-stratifying behavior of the AL-PHMS-X latex during film formation, the D-PHMS component—enriched at the coating surface due to its lower surface energy—effectively modulates the interfacial characteristics of the coating. Water contact angle (WCA) and water absorption rate are widely employed to evaluate such surface properties.³³

To minimize the influence of surface roughness on wettability measurements, coatings were prepared under controlled conditions with a uniform thickness of $80 \pm 5 \mu\text{m}$. As illustrated in Fig. 5, increasing the D-PHMS content from 0 to 8% resulted in a rise in the WCA from 55° to 110° , while the water absorption rate decreased significantly from 6.03 to 1.58%. These results confirm that the incorporation of D-PHMS promotes the formation of a self-stratified structure, leading to a transition in surface character from hydrophilic to hydrophobic.

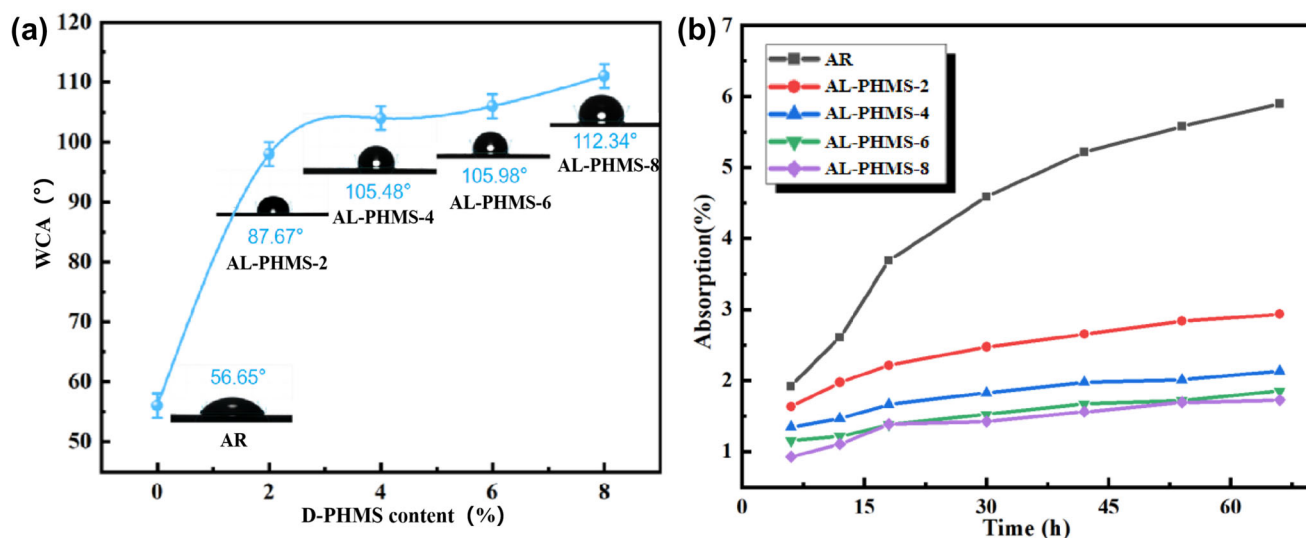


Fig. 5: The performance of the cured coatings varied with the content of D-PHMS (a) water contact angle; (b) water absorption rate

Furthermore, diiodomethane was used as a probe liquid to determine the contact angle, and the surface energy of the coatings was calculated according to the Wu model. The results are presented in Fig. 6. As the D-PHMS content increased, the wettability toward diiodomethane decreased, indicating a corresponding reduction in surface free energy from 43.5 ± 1 mN/m to 24.9 ± 1 mN/m. SEM observations confirmed that the coating surfaces were smooth and homogeneous, ruling out morphological effects on wettability measurements. These findings demonstrate that the copolymerization with D-PHMS effectively lowers the surface tension of the resin, thereby imparting hydrophobic characteristics to the coating.

The chemical and physical durability performance of the cured coatings

Owing to its intrinsically low surface energy, the cured coating exhibits pronounced hydrophobicity, making it a promising candidate for antifouling applications, as supported by previous studies.^{38,39} Nevertheless, for practical industrial deployment, exceptional durability remains an equally critical performance criterion alongside hydrophobicity.

In this section, AL-PHMS-6 was selected as a representative sample to evaluate the antifouling performance of the coating under a range of harsh and realistic conditions. Figure 7 systematically summarizes the results of these tests, which included oil

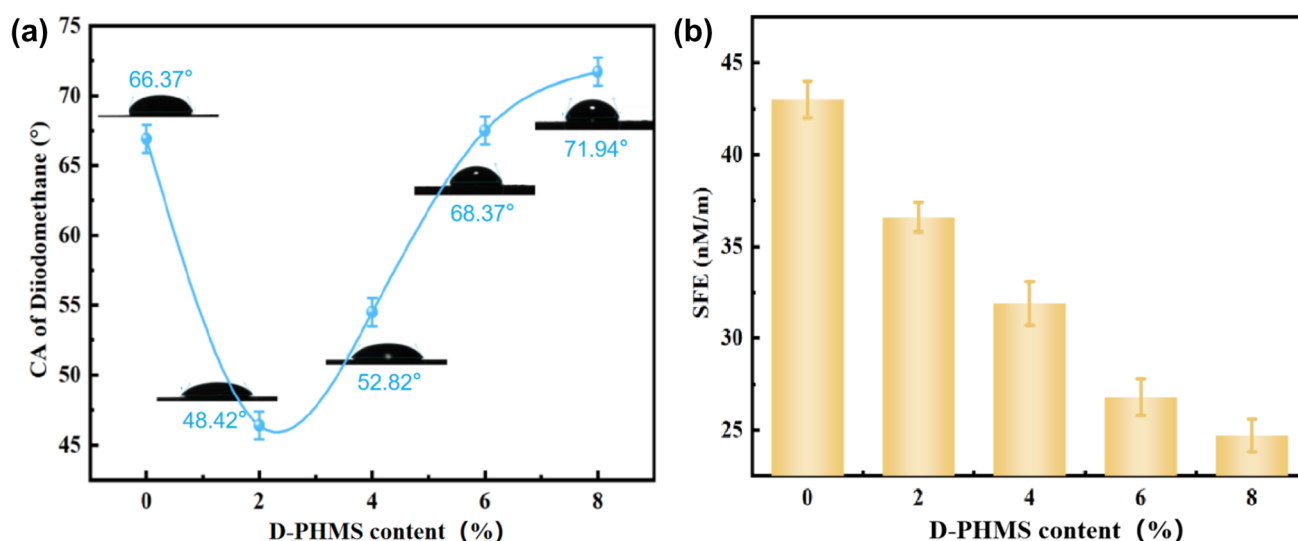


Fig. 6: The trend of the cured coatings varied with the content of DHMS (a) The contact angle by using diiodomethane as the probe liquid; (b) The surface free energy of the coatings

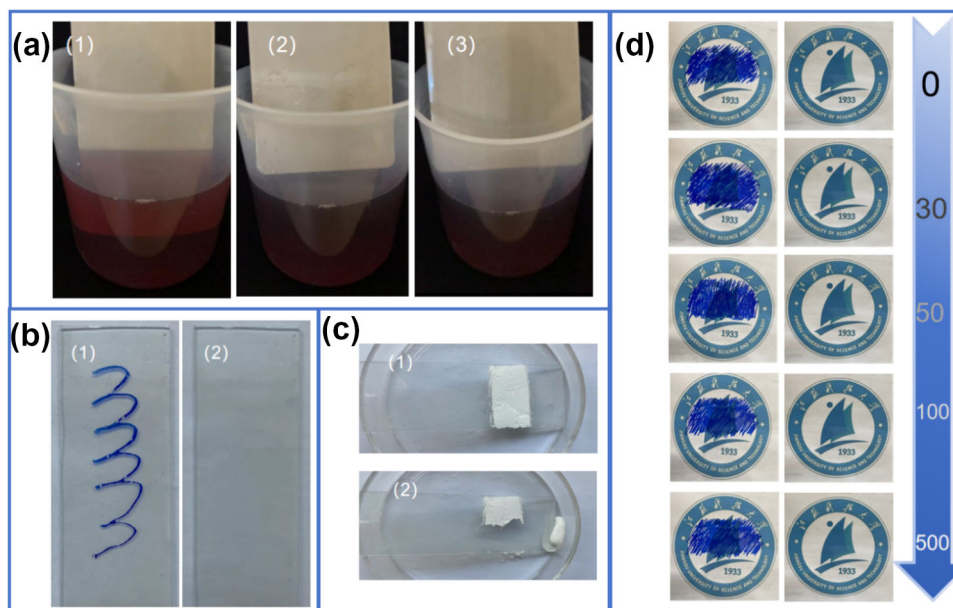


Fig. 7: The antifouling performance of the AL-PHMS-6 coating (a) after immersing in the oil bath at 120 °C for 2 h, (b) and (c) after flushing with boiling water for 30 s, and (d) after 0, 50, 150, 300 and 500 cycles of writing and wiping

immersion to simulate oil-rich industrial environments, boiling-water treatment to replicate high-temperature and high-humidity exposure, and cyclic wiping to mimic long-term mechanical wear. As shown in Fig. 7(a), the coated tinplate was first placed in an oil bath at 120 °C for 2 h (a_1). It was then immersed in red-dyed ethanol for 2 min (a_2). Upon removal, the ethanol rapidly contracted on the surface and slid off completely within 2 s (a_3), demonstrating the coating's strong liquid-repellent properties. Furthermore, when the coated glass slide was subjected to a continuous stream of boiling water for 30 s, the anti-graffiti performance remained unaffected, with no observable degradation (Fig. 7b₁–b₂). Subsequently, clay applied to the coating after boiling-water treatment could be easily rinsed off with a small amount of water without leaving stains (Fig. 7c), indicating excellent self-cleaning ability and stability under thermal and mechanical challenge.

In addition to antifouling and self-cleaning assessments, the coating's durability was further evaluated through repeated writing-and-erasing tests, as shown in Fig. 7(d). Even after 500 cycles, blue oil-based ink continued to exhibit characteristic bead-up behavior on the coating surface. Importantly, the surface remained entirely free of residue after each cleaning cycle. These results confirm the exceptional durability of the coating, underscoring its potential for long-term use in demanding industrial applications.

The corrosion resistance performance analysis

The corrosion resistance of the cured AL-PHMS-X coatings was comprehensively evaluated primarily by

electrochemical impedance spectroscopy (EIS), with Tafel polarization serving as an auxiliary method for a semi-quantitative comparison of corrosion rates among the different formulations.

TAFEL POLARIZATION MEASUREMENTS: Tafel polarization curves were recorded for the various coatings after 60 days of immersion in a 3.5 wt% NaCl solution (Fig. 8). The corresponding corrosion parameters, including corrosion current density (I_{corr}) and calculated corrosion rate (C.R.), are summarized in Table S1. A general trend was observed where the I_{corr} value decreased with increasing D-PHMS content up to 6 wt%, indicating a reduction in the

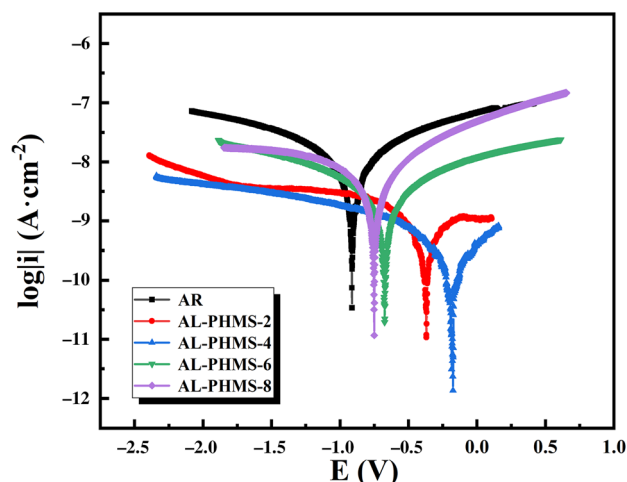


Fig. 8: Polarization curves of the different AL-PHMS-X coatings varied with the content of D-PHMS

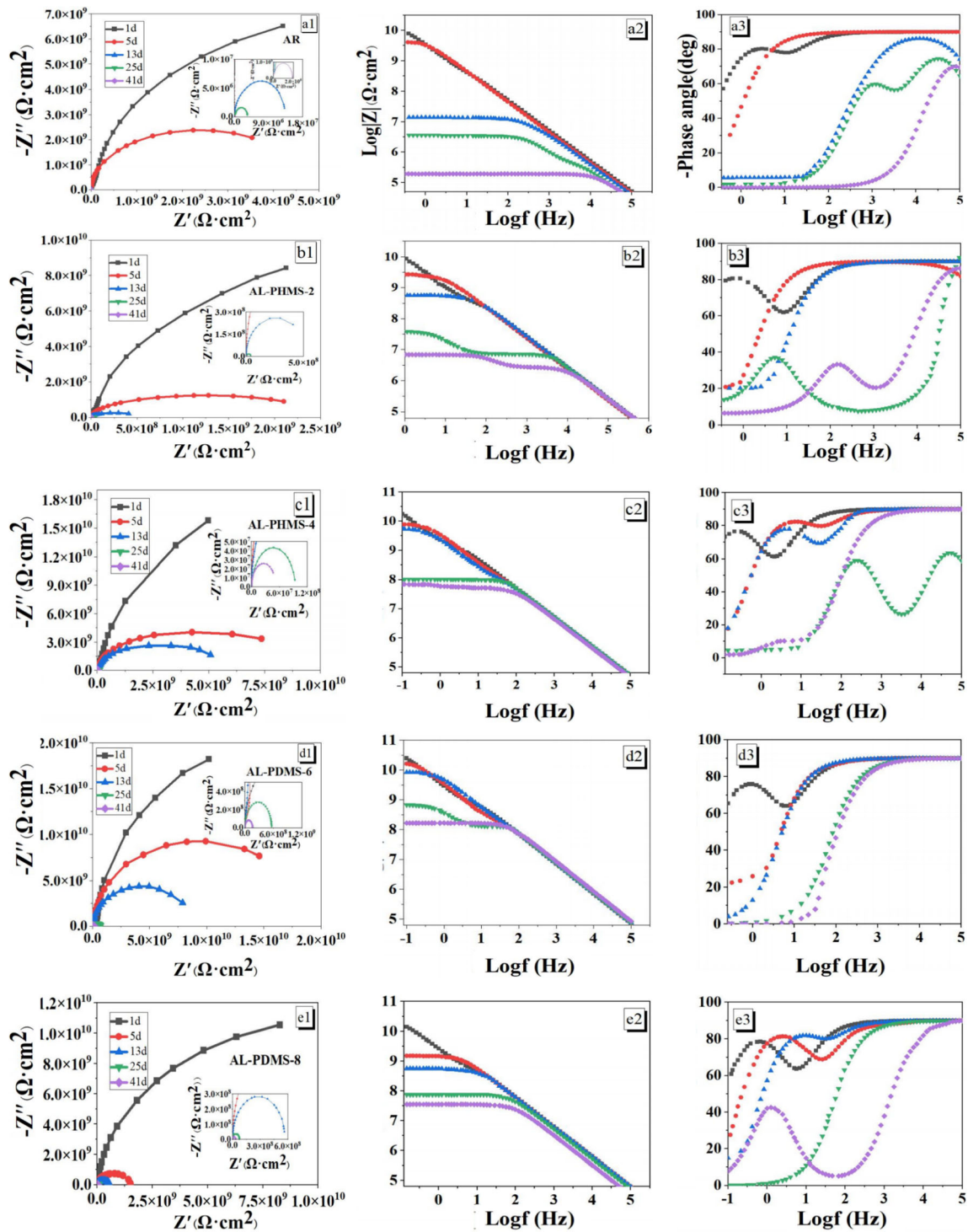


Fig. 9: (a1–e1) Nyquist plots, (a2–e2) bode plots and (a3–e3) Phase plots of various coatings in the corrosive medium after 1 d (black), 5 d (red), 13 d (blue), 25 d (green), and 41 d (purple). (a1–3 AR, b1–3 AL-PHMS-2, c1–3 AL-PHMS-4, d1–3 AL-PHMS-6 and e1–3 AL-PHMS-8). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

corrosion rate. This preliminary data suggests that the incorporation of D-PHMS enhanced the coating's barrier properties against corrosive agents. However, it is acknowledged that Tafel extrapolation on coated samples can be thickness-dependent and may not fully capture the complex degradation mechanisms of organic coatings.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) ANALYSIS: Given the limitations of Tafel tests for coated systems, EIS was employed as the principal method to provide a more in-depth and reliable assessment of the coatings' corrosion protection performance and their failure processes over time.

Figure 9(a₁–e₁) presents the Nyquist plots of the various coatings as a function of immersion time. The impedance arc radii of all coatings continuously decreased with prolonged immersion, reflecting progressive corrosion and a gradual decline in protective performance—a behavior commonly observed in coating systems. For the pure waterborne acrylic coating (WAC), the impedance arc diminished significantly, with the impedance modulus decreasing from $10^{10} \Omega \cdot \text{cm}^2$ to $10^7 \Omega \cdot \text{cm}^2$ after 13 days of immersion in 3.5 wt% NaCl solution, indicating a substantial reduction in charge transfer resistance. The equivalent circuit model fitted from the EIS data suggests that the coating was severely degraded, with the corrosive medium penetrating to the metal interface, facilitating corrosion and the dissolution of metal ions into the electrolyte. Incorporating D-PHMS into the acrylic resin markedly enhanced the corrosion resistance of the coatings. The AL-PHMS-6 coating maintained a comparatively large impedance arc throughout the testing period, and the equivalent circuit analysis indicated effective inhibition of corrosive medium penetration. Even after 41 days of immersion, the impedance modulus remained around $10^8 \Omega \cdot \text{cm}^2$,

demonstrating sustained barrier performance. However, the beneficial effect of D-PHMS is concentration-dependent. Excessive D-PHMS content (e.g., 8 wt%) adversely affects corrosion resistance due to incomplete encapsulation during emulsion polymerization, leading to inadequate copolymerization with acrylic monomers. The presence of unreacted D-PHMS oligomers may introduce structural defects, as evidenced by the slight reduction in the impedance arc observed for the AL-PHMS-8 coating in the later stages of testing.

Figure 9(a₂–e₂) displays the Bode plots for all coated samples, which exhibit trends consistent with the Nyquist plot results. The breadth of the phase angle plateau near -90° serves as an indicator of corrosion resistance, with a wider plateau corresponding to better protective performance. Notably, at a frequency of 0.01 Hz, the impedance modulus of the AL-PHMS-6 coating is approximately half an order of magnitude higher than that of the pure WAC coating. Moreover, the impedance value of AL-PHMS-6 remained stable over 41 days, maintaining around $10^8 \Omega \cdot \text{cm}^2$. In contrast, the other coatings showed a continuous and significant decline in impedance, with the low-frequency impedance modulus dropping from $10^{10} \Omega \cdot \text{cm}^2$ to $10^7 \Omega \cdot \text{cm}^2$, indicating inferior long-term anti-corrosion performance.

Figure 9(a₃–e₃) presents the phase angle plots as a function of immersion time. The width of the plateau near -90° is again indicative of the coating's barrier properties, where a broader plateau suggests more effective corrosion resistance. During the initial immersion period, all coatings exhibited relatively wide phase angle plateaus, demonstrating effective initial metal protection. However, in the middle and later stages, only the AL-PHMS-6 coating maintained a substantial plateau, confirming its retained corrosion resistance after 41 days of exposure.

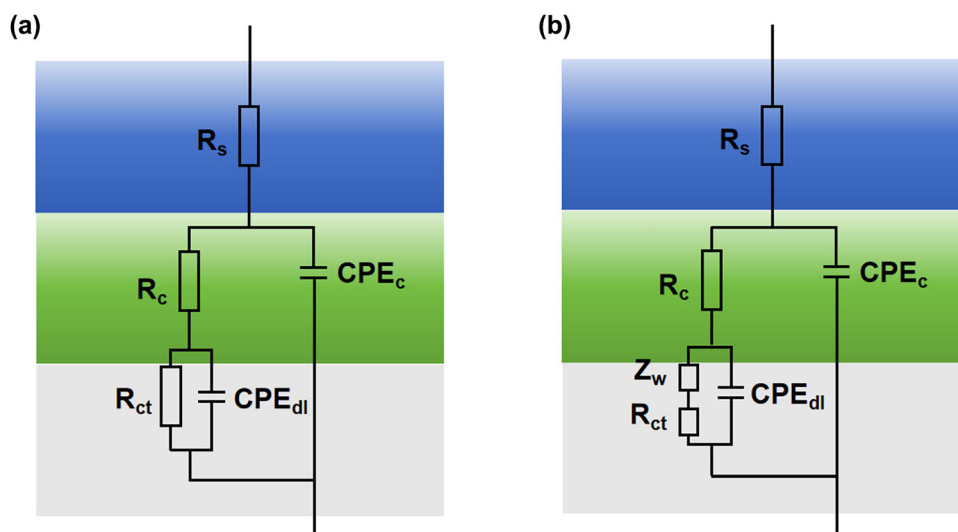


Fig. 10: Equivalent circuit diagram of EIS result fitting of (a) early corrosion and (b) late corrosion

During the testing, the overall process can be divided into two distinct stages: the initial penetration and degradation of the coating by corrosive media, followed by the electrochemical corrosion of the metal substrate. The corresponding equivalent circuits used for EIS fitting in each stage are presented in Fig. 10(a) and (b), respectively. In the equivalent circuits, R_s denotes the solution resistance, R_c represents the pore resistance of the coating, and R_{ct} corresponds to the charge transfer resistance. CPE refers to the coating capacitance, while CPE_{dl} represents the constant phase element associated with the metal corrosion process. W indicates the Warburg impedance. In the early stage of corrosion, the aggressive medium typically penetrates the coating through inherent micropores but has not yet reached the metal substrate. As the corrosion progresses to the later stage, the corrosive agents reach the metal interface and diffuse outward, ultimately leading to the formation of a new phase interface that replaces the original coating–metal boundary.

Conclusions

In summary, a hybrid latex was successfully synthesized via emulsion polymerization using acrylic monomers and modified silicone. Owing to differences in polarity and density, the components of the hybrid latex form a self-stratifying coating during film formation. Specifically, the low-surface-tension D-PHMS resin migrates to the air–film interface, imparting distinctive surface properties. The cured coatings exhibit favorable hydrophobicity, heat resistance, and corrosion resistance. Moreover, the use of water as a solvent enhances the environmental friendliness of the AL-PHMS-X system, facilitating its potential application in corrosion protection.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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