

Gallic acid-modified montmorillonite reinforced acrylic latex composite coatings: Enhanced mechanical and anticorrosion performances via barrier and interface passivation

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ABSTRACT

To mitigate the global economic loss exceeding \$1 trillion annually from corrosion, this study develops a multifunctional anti-corrosion composite coating by incorporating gallic acid-modified montmorillonite (D-MMT) into an acrylic latex (AL) matrix. The D-MMT, synthesized via ion-exchange, exhibited a significant expansion in interlayer spacing (from 1.270 nm to 1.680 nm) and enhanced dispersion within the polymer. At an optimal 4 wt% loading, the coating exhibited superior mechanical properties-increased hardness (from grade B to HB) and wear resistance-along with improved thermal stability (decomposition temperature elevated from 360 °C to 380 °C), attributed to hydrogen bonding between resin and nanofillers. Electrochemical analysis demonstrated exceptional corrosion protection, with low-frequency impedance modulus reaching $10^8 \Omega \cdot \text{cm}^2$ (two orders higher than pure AL) and corrosion current density reduced from 2.307×10^{-7} to $2.343 \times 10^{-9} \text{ A/cm}^2$ after 35-day immersion in 3.5 wt% NaCl. XPS and FESEM-EDS analyses revealed a post-damage interface passivation protection mechanism via gallic acid-mediated chelation-reduction, forming a dense passivation layer that effectively blocked active corrosion sites, evidenced by enriched Fe^{2+} ions (58.3 %) and reduced iron content (29.9 % vs. 74.81 % in AL) at damaged regions due to the strong reducing and chelating capabilities of gallic acid. This work provides a scalable strategy for designing coatings with integrated barrier, mechanical, and self-healing functionalities for industrial applications.

1. Introduction

Metal corrosion represents a critical factor in material failure, incurring global economic losses exceeding \$1 trillion annually while simultaneously triggering catastrophic safety risks and environmental hazards [1,2]. Fundamentally, corrosion is an electrochemically driven process governed by thermodynamics. At the metal interface, corrosive agents, such as O_2 and H^+ , act as depolarizers, facilitate spontaneous transition from the high-energy metallic state to low-energy corrosion products through electrochemical reactions that lower activation energy barriers [3,4].

Coating has emerged as the mainstream anti-corrosion technology

owing to its straightforward process in application and its controllable costs [5]. However, pure polymer coatings suffer from limitations such as microporous leakage and inherent permeability defects [6]. To overcome these bottlenecks, the introduction of multifunctional inorganic fillers (e.g., montmorillonite, mica powder, zinc phosphate) is essential for constructing composite coating systems [7,8]. Current research focuses on synergistic reinforcement mechanisms of fillers. By precisely tailoring their dimensional morphology, e.g., 2D montmorillonite nanosheets, and surface chemistry, e.g., controlled release of corrosion-inhibiting ions from zinc phosphate, these fillers integrate multi-level protective functionalities, including physical barrier, chemical passivation, and self-healing capabilities [9–11]. This integrated

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approach ensures comprehensive protection for metal substrates in their lifecycles under demanding service conditions, such as high salinity and mechanical stress, representing a persistent innovation direction in advanced design of anti-corrosion coatings [12,13].

Montmorillonite (MMT) is conventionally utilized as a thickening agent to regulate coating viscosity, yet its mechanisms in corrosion protection remain inadequately explored [14,15]. The nanosheet structure of MMT forms a physical network within the coatings, which acts as a barrier, forcing corrosive media (e.g., H_2O , Cl^-) to traverse a circuitous path and significantly prolonging permeation routes, which is a phenomenon termed as the “labyrinth effect” [16–18]. Concurrently, exchangeable interlayer cations (e.g., Na^+ , Ca^{2+}) enable the ion-exchange loading of corrosion inhibitors (e.g., zinc salts, cerium salts), facilitating controlled release, which is triggered by the corrosive microenvironment [19,20]. This endows coatings with active protection and self-healing capabilities. When embedded as a filler in resin matrices, MMT synergistically enhances mechanical strength [21], wear resistance [22], barrier properties [23], and hydrophobicity of a coating. For example, the ES/APDMS/MMT- SiO_2 composite coating, developed by Zhang [24], exhibits exceptional anti-corrosion performance. As validated by potentiodynamic polarization and electrochemical impedance spectroscopy, it features a notably low corrosion current density ($1.6 \times 10^{-10} \text{ A cm}^{-2}$) and a high protection efficiency (99.999 %).

Beyond the incorporation of nanofillers, loading corrosion inhibitors onto MMT enables the fabrication of anti-corrosion composite coatings that exhibit dual protective functionalities, namely, physical barrier action and self-healing capability. For example, Chen et al. [25] synthesized urushiol titanium polymer-intercalated montmorillonite (UTPOMMT) via in-situ polymerization, followed by its incorporation into epoxy resin (EP) to yield the UTPOMMT/EP composite coating. This approach facilitates the exfoliation of MMT within the epoxy matrix and promotes a more compact packing structure, thereby enhancing the barrier properties of the coating. Additionally, the presence of urushiol contributes to the improved corrosion resistance of the coating system. Cui [26] loaded benzimidazole, which possesses both anti-fouling and anti-corrosion properties, onto montmorillonite through cation exchange, resulting in the synthesis of a 2D nanofiller (GB@MMT). The incorporation of GB@MMT significantly enhances the corrosion protection performance and adhesion strength of the coating. Furthermore, upon artificial induction of defects in the coating, a stable “scar” formation is observed after immersion, enabling the realization of self-healing behavior. This work provides novel insights into the application of MMT in organic coatings.

The present study employs gallic acid (GA), a prototypical organic corrosion inhibitor with low toxic [27–29], to undergo a salification reaction with *N,N*-dimethylstearylamine (DMSA) prior to being utilized for modifying montmorillonite (MMT) via an intercalation reaction. The overarching objective is to elucidate the interaction mechanism between the GA modifier and MMT, delineate the pathways through which it effectively enhances the homogeneous dispersibility of MMT within the waterborne AL coating matrix, and thereby achieve the functional modification of the polymer coating. This research focuses on two pivotal dimensions: assessing the barrier efficacy of the multi-layered physical barriers constructed by modified MMT against brine permeation in corrosive media; and unraveling the reparative functionality of the gallic acid corrosion inhibitor on the low-carbon steel substrate.

2. Experimental section

2.1. Materials

Gallic acid (Ga, C.P.) was obtained from Xi ‘an Yanhao Biotechnology Co., Ltd. Montmorillonite (MMT) powder was taken from Yousuo (China). *N,N*-Dimethylstearylamine (DMA18, C.P.), Ethanol (A.R.), Diethylene glycol methyl ether (DEGME, C.P.), Ethylene glycol monobutyl ether (EGBE, C.P.) and Hexyl hydride (N-hexane, C.P.) were

obtained from Shanghai Maclean Biochemical Technology Co., Ltd. Tetrabutylammonium bromide (TBAB, C.P.) was purchased from Guangdong Yuanfeng Chemical Reagent Co., Ltd. Ammonium persulfate (APS, A.R.) was obtained from China Pharmaceutical Group Chemical Reagent Co., Ltd. Methacrylic acid (MAA, C.P.), Styrene (St, C.P.), Iso-octyl acrylate (2-EHA, C.P.) and Methacrylate (MMA, C.P.) were obtained from Jiangsu Qiangsheng Functional Chemical Co., Ltd. Anionic emulsifier (ABEX DBR-Z, Solvay), nonionic emulsifier (Triton®X-405, Merck), film-forming aid (Alcohol ester 12, Macklin), and flash rust inhibitor (NaNO_2 , AR) were purchased from commercial sources.

2.2. Preparation of modified-MMT

2.2.1. Synthesis of *N,N*-Dimethylstearylamine gallate (DMSAG)

N,N-Dimethylstearylamine and gallic acid (molar ratio 1:1) were dissolved in a mixed solvent of ethanol/EGBE(1:1, v/v). The solid content was maintained at 20 wt%, and tetrabutylammonium bromide (TBAB, 1 wt% of the total mass) was added as a catalyst. The reaction mixture was stirred under reflux conditions. The detailed synthetic procedure is provided in the Supporting Information. The product was named as *N,N*-Dimethylstearylamine gallate (DMSAG).

2.2.2. Preparation of DMSAG-modified montmorillonite (D-MMT)

MMT was dispersed in deionized water to prepare a dispersion with a solid content of 0.1 g/mL. The dispersion was stirred at 80 °C for 1 h to ensure thorough dispersion of MMT in the aqueous phase. Subsequently, the DMSAG prepared above was added to the MMT dispersion, and the mixture was continuously stirred at 80 °C for 5 h. The reaction product was obtained by suction filtration, and then was washed with ethanol, and vacuum dried at 50 °C for 24 h, yielding DMSAG-modified MMT (D-MMT). To investigate the effect of DMSAG on bentonite structure and properties, mass ratios of MMT to DMSAG were varied as 5:1, 4:1, 3:1, 2:1, and 1:1. The samples are designated D/MMT-X, where X represents the mass ratio of MMT to DMSAG (e.g., X = 5 for 5:1 ratio).

2.3. Preparation of D-MMT doped acrylic latex (D-MMT/AL)

Synthesis of AL employed methyl methacrylate (MMA) and styrene (St) as hard monomers, 2-ethylhexyl acrylate (2-EHA) as the soft monomer, and methacrylic acid (MAA) as the functional monomer, ABEX DBR-Z and Triton® X-405 served as the anionic and nonionic emulsifiers, respectively, with ammonium persulfate (APS) acting as the water-soluble initiator. The glass transition temperature (T_g) of the polymer was set at 25 °C. The AL was synthesized via a seeded emulsion polymerization methodology.

D/MMT was then added to the synthesized AL at a fixed stoichiometric ratio. After mechanical stirring for 30 min, 0.1 wt% sodium nitrite (NaNO_2) and 5 wt% Texanol were added as anti-flash rust and film-forming additives, respectively. The mixture was stirred to homogeneity, yielding the modified bentonite-doped AL. To systematically evaluate the effect of D/MMT content on composite coatings, its concentration was adjusted to 2–8 wt% of the AL solid content. The resulting samples were denoted as D-MMT-X/AL-Y% (Y = 2–8), with Y representing the mass fraction of D-MMT in the composite coatings.

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 D-MMT/AL 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 60 μm on silica glasses.

2.4. Characterizations

FTIR spectroscopy was performed on a Nicolet iS10 Fourier Transform Infrared Spectrometer (Thermo Electron Corporation, USA). Spectra of the samples were recorded in the range of $4000\text{--}500\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . XRD was performed on Bruker's D8 Advance X-ray diffractometer. The Cu K α -ray ($\lambda = 0.154\text{ nm}$) was used as the energy source, with a test range of 5° to 85° and a scanning rate of $5^\circ/\text{min}$. The thermal stability of the powder filler and coatings was analyzed by a Perkin Elmer's Diamond TG-DTA thermogravimetric analyzer. The correlation between the segmental motion of polymers and temperature was carried out by the Diamond DSC 8000 Differential Scanning Calorimeter, and the heating-cooling cycles were conducted between -10°C and 100°C at a rate of $10^\circ\text{C min}^{-1}$ under a 50 mL min^{-1} flow of nitrogen. FESEM-EDX analyses were performed on a Hitachi S4700 (Tokyo, Japan) with a field emission gun at 13.0 kV and $25\text{ }\mu\text{A}$. To facilitate cross-sectional analyses, coatings were cut in liquid nitrogen. The toughness of coatings was evaluated using a QTY-32 type paint film bending tester (State-owned Tianjin Weida Testing Machine Factory) according to GB/T 1731–2020. Impact tests of coatings were conducted using a BGD 302 tubular paint film impactor according to

GB/T 20624.2–2006. The hardness of coatings was assessed by the hardness method using pencil, according to GB/T 6739–2006 method. The Wear resistance tests of coatings were conducted using JM-V rotate the friction rubber wheel according to ISO 7784-2:1997. The anti-corrosion property of coatings was tested using the American Gamry electrochemical workstation. A 3.5 % NaCl solution was used as the corrosion medium. XPS was performed on the Nexsa X-ray photoelectron spectrometer combined with high-resolution scanning technology, to investigate the elemental composition and the distribution of valence states in a scratch of coating, and high-resolution scanning was conducted for elements that existing in the material. The test depth of a sample is 5 nm . For Tafel polarization curve tests, the polarization curve scan rate was 1 mV/s , and the dynamic potential scan range was $-1.5\text{--}0\text{ V}$ (relative to open circuit potential). EIS was performed on the Chi604E (Shanghai Chenhua Instrument Co., LTD). Carbon steel was used as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum sheet electrode ($1 \times 1\text{ cm}^2$) as the counter electrode. Electrochemical tests mainly include electrochemical alternating current impedance (EIS), and dynamic potential polarization curves, etc. The frequency range for EIS testing is 10^5 Hz to 10^{-2} Hz .

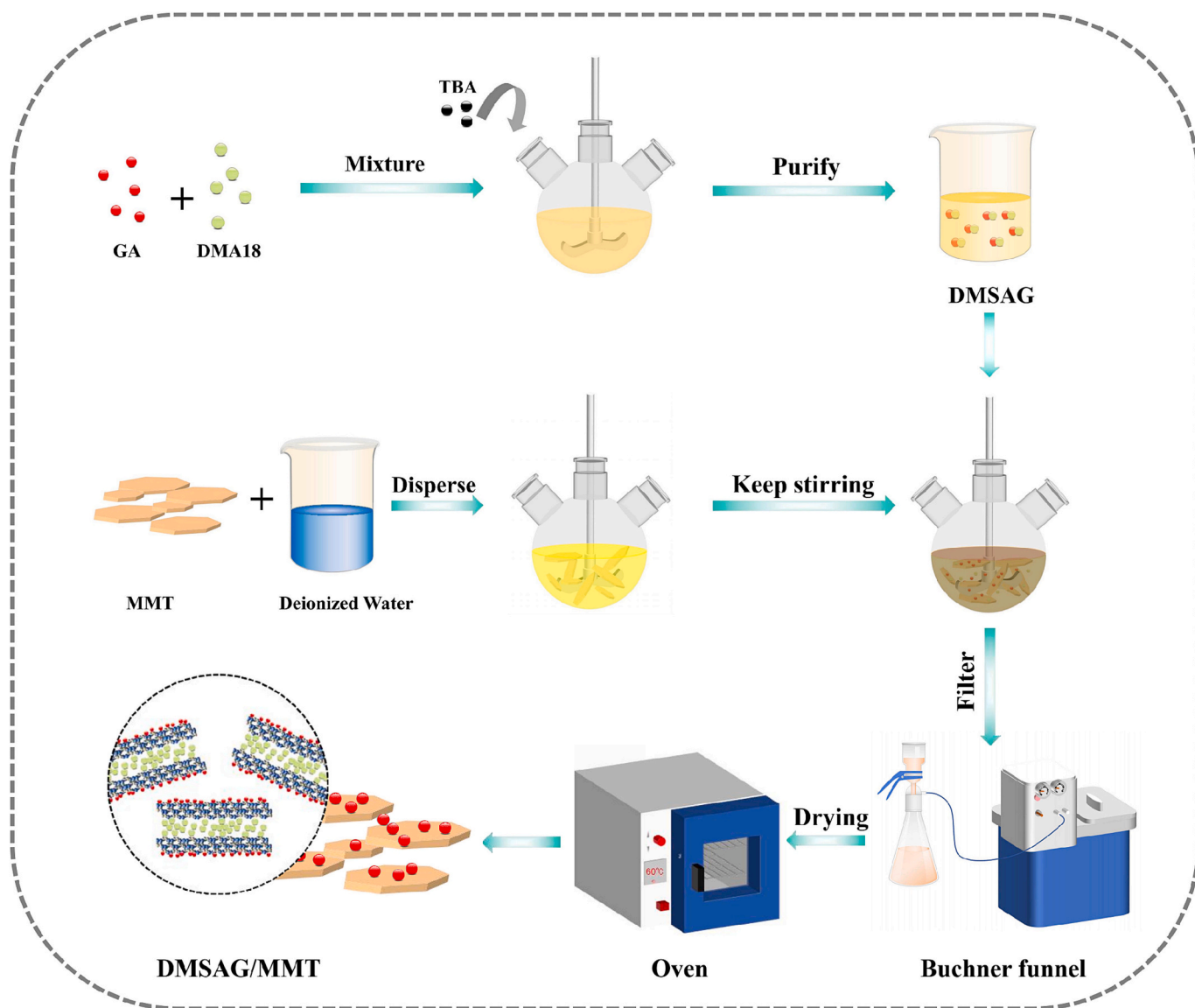


Fig. 1. Synthesis of DMSAG and D-MMT.

3. Results and discussion

3.1. Analysis of the structure and properties of D-MMT and its intermediates

To confirm that DMSAG had been successfully grafted onto MMT and exerted structural modifications, a series of characterization techniques were employed for analysis.

Fig. 1(a) displays the FTIR spectra of different raw materials and the obtained D-MMT. The IR spectrum of intermediate DMSAG exhibits carboxylate vibrations at 1630 cm^{-1} (ν_{asCOO} , indicating charge delocalization) and 1420 cm^{-1} (ν_{sCOO}), confirming the formation of ionic bond. In addition, the disappearance of the 1720 cm^{-1} peak (assigned to free gallic acid C=O stretching) provides conclusive evidence for complete neutralization and salt formation. Comparison of the MMT and D-MMT spectra reveals new absorption peaks at 2916 cm^{-1} and 1470 cm^{-1} in D-MMT. These new peaks indicate the successful intercalation of DMSAG into MMT interlayer space via an ion-exchange reaction. Collectively, these results demonstrate that DMSAG (an ammonium salt) was synthesized by acid-base neutralization of GA and *N,N*-dimethylstearylamine and subsequently intercalated into MMT through ion-exchange, achieving organic modification of MMT.

To investigate the effect of DMSAG intercalation on the crystal structure of MMT, XRD measurement was employed to analyze both pristine and modified samples. The interlayer spacing (d_{001}) was calculated using the Bragg equation ($2d\sin\theta = n\lambda$). The average distance between montmorillonite (MMT) layers is denoted as d , where θ represents the Bragg angle (half the diffraction angle), and λ is the wavelength of incident X-rays ($\lambda = 0.154\text{ nm}$). The diffraction order n is set to 1. As shown in Fig. 2(b), the (001) diffraction peak of pristine MMT appears at a higher angle, corresponding to an average d_{001} value of 1.270 nm . After modification with DMSAG, the (001) peak shifts significantly toward lower angles, with the magnitude of this shift increasing proportionally to the DMSAG content. For DMSAG-1, the d_{001} value expands to 1.680 nm . These results confirm that DMSAG successfully intercalated into the MMT interlayers, inducing lattice expansion and validating the effectiveness of the intercalation modification.

Fig. 2(c) displays the TGA curves of pristine MMT and D-MMT at varying modifier contents. For pristine MMT, the initial weight loss (5–8 %) near $100\text{ }^{\circ}\text{C}$ is attributed to the removal of both adsorbed and crystalline water from the interlayer spaces. A secondary weight loss ($\approx 3\%$) observed at $500\text{ }^{\circ}\text{C}$ corresponds to structural collapse and a complete elimination of hydroxyl groups ($-\text{OH}$). The thermal degradation of D-MMTs proceeds through three distinct stages: first, a rapid weight loss occurs between $120\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$, with the extent of loss correlating with DMSAG content (e.g., 30 % for DMSAG-1 vs. 8 % for pristine MMT), attributed to thermal decomposition of surface-adsorbed gallate ions;

second, stepwise weight loss initiates at $\sim 375\text{ }^{\circ}\text{C}$, driven by decomposition and volatilization of intercalated organic amine ions; third, progressive weight loss above $500\text{ }^{\circ}\text{C}$ reflects degradation of the MMT crystal lattice and elimination of residual hydroxyl groups, aligning with the thermal profile of unmodified MMT. In addition, taking pure MMT and D-MMT-1 as examples, their corresponding DTA analyses further elucidate the differences in their thermal decomposition behavior, as shown in Fig.S1 (Supporting Information), demonstrating the effective intercalation and modification of MMT by DMSAG.

Based on the analysis of the above three tests, the following conclusions can be drawn. The carboxylic group of gallic acid reacts with the amino group of octadecyl dimethyl tertiary amine through a catalyzed acid-base neutralization, forming ammonium salt. This ammonium salt undergoes ion-exchange with montmorillonite (MMT), facilitating the salt's intercalation into the clay interlayers. The process increases the interlayer spacing of MMT, while the ammonium salt's long alkyl chain enhances compatibility with polymer matrices. Gallic acid anions adsorb onto MMT through two primary mechanisms, cation bridging and hydrogen bonding. In cation bridging, residual interlayer cations (e.g., Ca^{2+} , Mg^{2+}) form bridges between the clay surface and the gallic acid anions, resulting in "gallic acid anion-cation-MMT" complexes. Hydrogen bonding occurs when oxygen atoms within the gallic acid anions form hydrogen bonds with hydroxyl groups on the MMT surface [30]. This modification facilitates uniform dispersion of gallic acid throughout the MMT structure, thus enabling targeted modification of polymer coatings. The resulting hybrid material consequently combines the barrier properties of MMT with the functional activity of gallic acid, leading to enhanced mechanical properties and improved anti-corrosion performance in coating applications.

Within a specific compositional range, the interlayer spacing of MMT expands linearly with the increase in DMSAG concentration. This expansion enables the effective nanoscale dispersion of MMT, which in turn significantly enhances the composite's mechanical properties, thermal stability, barrier characteristics, and flame retardancy. Thus, D-MMT-1 was chosen as the representative sample to be incorporated into an AL matrix, facilitating subsequent investigations into its impact on the performance of composite coatings.

3.2. Morphological and structural analyses of raw MMT and D-MMT and their corresponding composite coatings

The surface and internal structure of pristine montmorillonite (MMT) and D-MMT powder samples (with D-MMT-1 as the representative example) were characterized using FESEM. Fig. 3(a) reveals that the pristine MMT particles exhibit a tightly agglomerated morphology, forming a continuous and relatively smooth surface. In striking contrast, the D-MMT (Fig. 3b) displays marked alterations: Intercalation of the

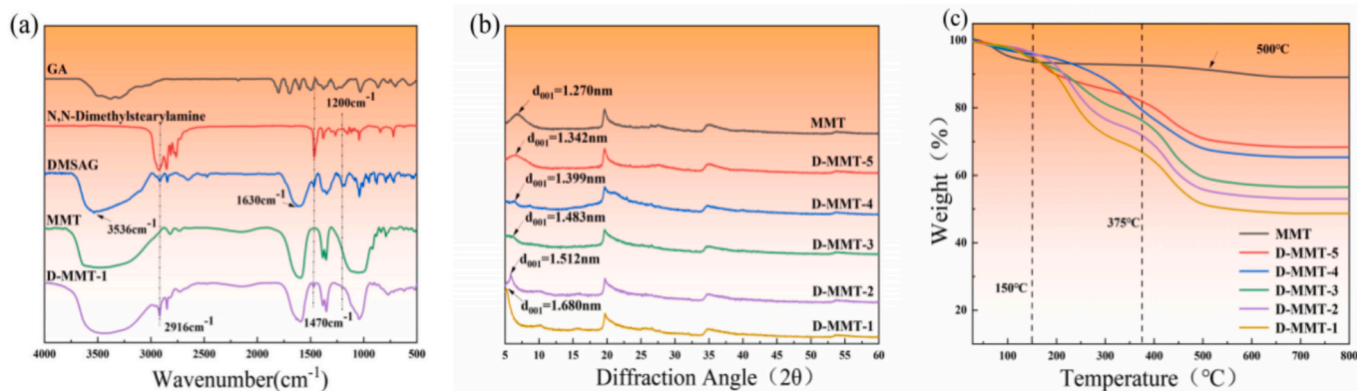


Fig. 2. (a) FTIR spectra; (b) XRD patterns; (c) thermogravimetric curves (TG); and (d) derivative thermogravimetric (DTG) curves of both the pristine materials used for D-MMT synthesis and the resultant organomodified D-MMT.

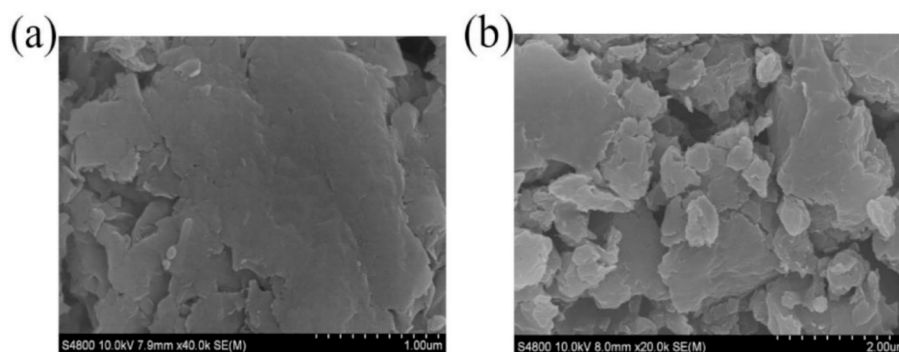


Fig. 3. FESEM images of (a) raw MMT; (b) D-MMT (D-MMT-1 was taken as the example).

quaternary ammonium cations expands the interlayer spacing, resulting in a loosely packed yet ordered stacking structure accompanied by distinct book-like separation in localized regions. Furthermore, surface coverage by gallic acid ions induces a significant roughening of the particle morphology. Collectively, these structural transformations indicate a shift in the modified filler from a predominantly microporous configuration to a bidimensional, interpenetrating porous network featuring both micropores and mesopores [31]. Fig.S2 displays the FESEM elemental mapping of D-MMT-1 powder. The homogeneous distribution of the core constituents of MMT (Si, Al, Mg, and O) confirms the inherent mineral structure. Notably, a uniform signal of C and N, which are the characteristic organic elements of DMSAG, is observed across the MMT filler surface. This provides direct evidence for the effective intercalation and modification of MMT by quaternary ammonium cations, which concomitantly reduces particle aggregation. Furthermore, gallate ions are stabilized on the MMT surface via hydrogen bonding or bridging interactions, thereby influencing both the filler morphology in paint applications and the resulting coating performance.

Subsequently, representative clay materials, MMT and D-MMT-1, were introduced into the AL at 4 wt% solid content. After homogeneous dispersion, the mixture was spray-coated onto the substrate and cured to form films. The surface and cross-sectional morphologies of both the pure polymer latex film and composite films are shown in Fig. 4.

The cured coatings formulated with AL (free of any fillers) exhibit smooth surface and uniform fracture patterns, which are a typical morphology of brittle fracture. Fig. 4(b) displays the composite coatings with unmodified MMT incorporated into the AL matrix. This incorporation results in significant agglomeration, poor dispersion, persistence of the stacked crystalline structure without exfoliation, and substantial

interfacial voids. This poor dispersion and interfacial incompatibility stem from strong hydrogen bonding and electrostatic interactions (e.g., between K^+/Na^+ interlayer cations) within the MMT galleries. These forces prevent spontaneous polymer chain intercalation, preserving the stacked layers of MMT. Additionally, the hydrophilic hydroxyl groups ($-OH$) on the MMT surface exhibit poor compatibility with the hydrophobic polymer matrix. Due to the intercalation modification of organic ammonium salts, the doped D-MMT-1 enables nanoscale dispersion, exfoliation of silicate layers, and enhanced interfacial compatibility within the polymer resin, forming a robust nanocomposite system with strong interfacial bonding interactions. This outcome arises from the substitution of inorganic interlayer cations (e.g., Na^+ , K^+) by organic modifiers. The long-chain alkyl or aromatic groups reduces interlayer polarity while establishing hydrophobic interactions or chemical bonding with the polymer matrix. The incorporation of D-MMT yields an irregular fracture surface in the cross-section of the coating. Notably, the D-MMT generates a “maze effect” within the coating. The exfoliated nanosheets create multi-layered physical barriers. When corrosive species penetrate the coating, these barriers force diffusion along tortuous paths rather than direct penetration, significantly extending the penetration time—the essence of the “maze effect.” This mechanism impedes contact between corrosive media and the metal substrate in anticorrosive coatings.

3.3. The effect of doped D-MMT on the thermodynamic properties of composite coatings

The thermodynamic properties of coatings constitute the fundamental basis for their mechanical behavior, environmental adaptability, and functional durability [32].

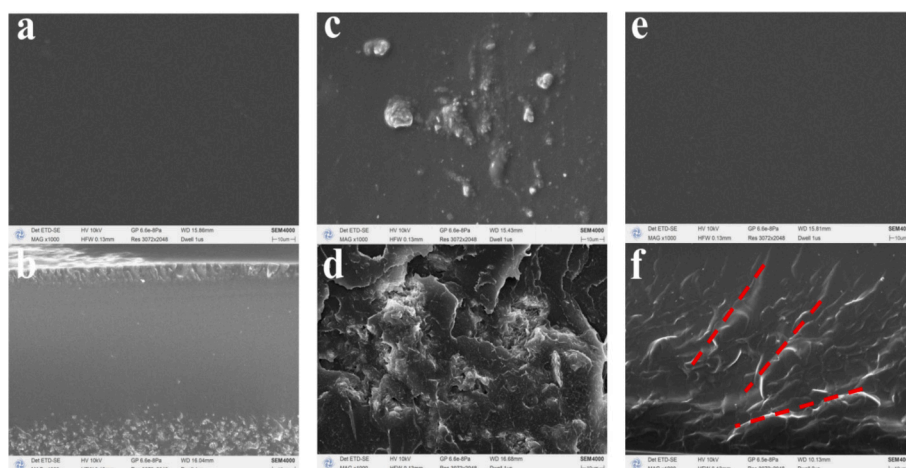


Fig. 4. The surface and cross-sectional morphologies of different coatings observed by FESEM: (a) pure AL; (b) MMT/AL-4 %; (c) D-MMT-1/AL-4 %.

Fig. 5(a) displays the TGA curves of the AL coating and composite coatings with various D-MMT/AL content (D-MMT-1 was used as the tested example). All samples exhibit a minor mass loss near 100 °C, which is attributed to the evaporation of residual water from emulsion synthesis and coating preparation. At around 360 °C, the pure AL coating shows a rapid degradation plateau. Notably, the thermal decomposition temperature of the D-MMT-1-AL-4 % increases significantly from 360 °C to 380 °C. This enhancement is ascribed to hydrogen bonding and polar interactions between the nanofillers and the resin matrix [33]. When subjected to testing, the high-temperature resistance of MMT retards the decomposition of the polymeric components. By 450 °C, thermal decomposition of resin is essentially completed. Due to the exceptional thermal stability of MMT, no substantial mass loss occurred within the tested temperature range, and the final residual mass of the coatings correlated with the filler loading.

Furthermore, Fig. 5(b) presents the DSC data of the composite coatings, to understand the relationship between the segmental motion of the polymeric chains and the presence of D-MMT. The glass transition temperature (T_g) of the pure AL coating was measured at around 25 °C. Notably, upon the incorporation of D-MMT, the T_g of the coating increased, and this increase was further enhanced with higher loadings of the modified nanofiller. Specifically, at a D-MMT/AL content of 8 wt %, the T_g reached 33.2 °C. D-MMT, characterized by its lamellar crystal structure, promotes uniform dispersion within the coating matrix. Consequently, hydrogen bonding and polar interactions between the D-MMT layers and the polymer chains effectively confine the polymer segments. This confinement restricts the molecular motion upon heating, leading to the observed elevation in the T_g of the polymer coatings.

3.4. The effect of doped D-MMT on the mechanical properties of composite coatings

The mechanical properties of coating determine its ability to withstand applied stress, resist impact, and undergo deformation during service [34,35]. Incorporating composite fillers represents a common and effective strategy for enhancing the mechanical properties of the resin matrix. Hardness, toughness, impact resistance, and wear resistance serve as key indicators of a material's mechanical characteristics. All experimental datasets underwent triplicate verification to ensure the reliability of averaged effective values..

As shown in Table 1, the mechanical properties of the composite coatings follow a linear relationship with the increase in the D-MMT-1

Table 1

Mechanical properties of cured coatings of AL and the D-MMT/AL composite coating.

	AL	D-MMT-1/ AL-2 %	D-MMT-1/ AL-4 %	D-MMT-1/ AL-6 %	D-MMT-1/ AL-8 %
Hardness	B	HB	HB	HB	H
Toughness(mm)	1.5	2	2	2.5	2.5
Impact resistance (kg·cm)	35	35	35	30	25

loading. Specifically, coating hardness increases monotonically, which is attributed to the homogeneous dispersion of lamellar D-MMT-1 crystallites within the polymer matrix and interfacial interactions (e.g., hydrogen bonding and van der Waals forces) between the inorganic filler and organic resin. These interactions restrict the mobility of polymer chain, thereby enhancing the coating's compressive strength. In contrast, both flexibility and impact resistance exhibited a linear decline, collectively indicating a transition of the composite from a tough to a brittle state. These results suggest that D-MMT incorporation modulates molecular chain dynamics via filler-matrix interfacial interactions, thereby influencing the balance of mechanical properties.

The inclusion of nano-fillers also significantly modulates the wear resistance of the cured coatings. Fig.S2 depicts the trend of wear rate versus the number of friction cycles for the various composite coatings. At a D-MMT-1 loading of 2 wt%, the composite coating exhibits significantly superior wear resistance compared to the AC coating. The optimal wear resistance is achieved at 4 wt% D-MMT-1, where the mass loss rate reaches its minimum value. However, further increasing the filler content to 6 wt% leads to a significant rise in the mass loss rate. This deterioration is attributed to the brittleness induced by excessive MMT inclusion, which compromises the coating's flexibility and, consequently, its wear resistance. Notably, the D-MMT-1/AL-8 % composite coating suffers a mass loss rate exceeding that of the AL coating, indicating the most pronounced degradation in wear performance. Although homogeneous dispersion of the nanofiller D-MMT within the coating leads to a decrease in flexibility and impact resistance, it effectively enhances coating hardness and wear resistance. Therefore, by accepting a moderate trade-off in flexibility and impact resistance, a coating system possessing both high hardness and high wear resistance can be attained. These findings confirm the beneficial role of

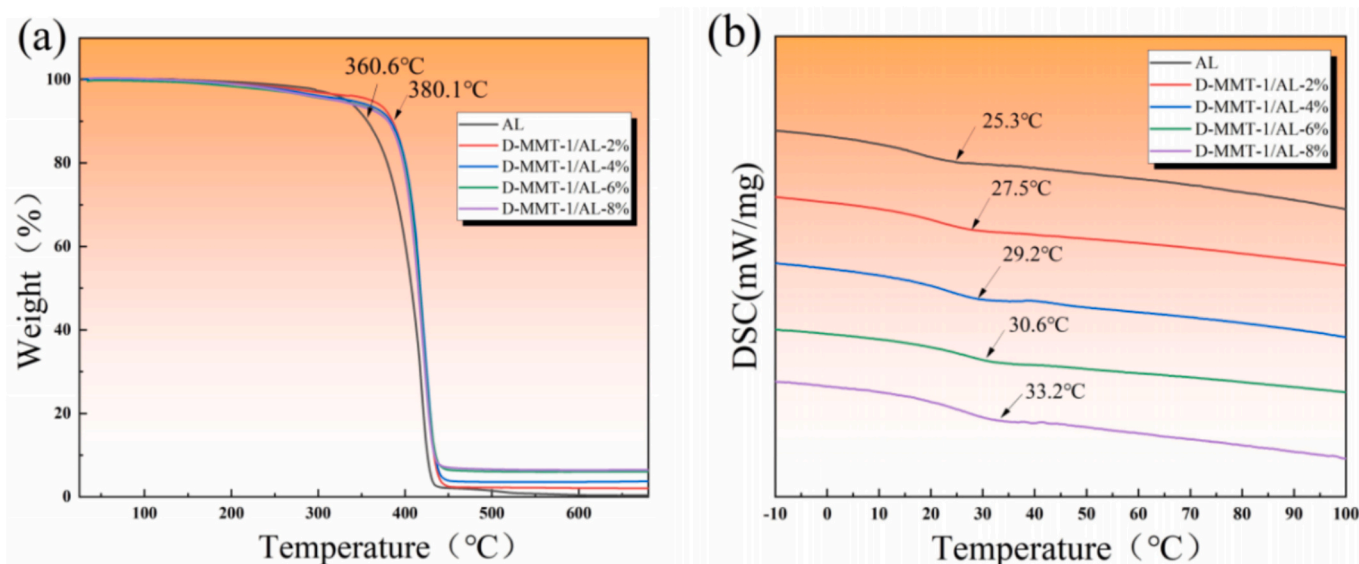


Fig. 5. (a) TGA curves and (b) DSC curves of AL coatings and composite coatings doped with different contents of D-MMT(D-MMT-1 was used as the example).

incorporating D-MMT in enhancing the overall mechanical properties of the coatings. Considering the comprehensive performance metrics, the composite coating D-MMT-1/AL-4 % demonstrates the optimal mechanical performance, establishing it as the preferred formulation for this system.

3.5. The effect of doped D-MMT on the anticorrosion properties of composite coatings

3.5.1. Characterization of the corrosion inhibition behavior of D-MMT

To validate the corrosion inhibition efficacy of gallic acid following its intercalation modification within montmorillonite (MMT) fillers, two liquid samples were prepared: one containing pristine MMT and the other incorporating D-MMT-1. Both samples were dispersed in an aqueous phase at a solid content of 100 mg/L, followed by the addition of NaCl to achieve a concentration of 3.5 wt%. Q235 steel electrodes were immersed in these test solutions for 24 h, after which electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were recorded.

Fig. 7(a)–(c) presents a comparison of the Nyquist plots, Bode magnitude plots, and Bode phase angle plots for the two sample sets. The equivalent circuit models employed for the EIS analysis are illustrated in Fig.S3(a) and (b). The EIS results demonstrate that the solution containing 100 mg/L D-MMT-1 ($|Z|_{0.01\text{Hz}} = 878\Omega\text{cm}^2$, $f_b = 0.09\text{ Hz}$) exhibited a higher low-frequency impedance modulus and a lower characteristic breakpoint frequency compared to the solution containing 100 mg/L MMT ($|Z|_{0.01\text{Hz}} = 561\Omega\text{cm}^2$, $f_b = 0.12\text{ Hz}$). Furthermore, analysis of the Bode magnitude plots (Fig. 7(b)) reveals that the D-MMT sample possesses a substantially higher polarization resistance ($R_{ct} = 942\Omega\text{cm}^2$) than the 3.5 wt% NaCl solution as the blank ($R_{ct} = 602\Omega\text{cm}^2$).

Fig. 8(a) displays the potentiodynamic polarization curves for Q235 carbon steel immersed in the corrosive solution for 24 h, and Fig. 8(b) shows the corresponding corrosion current densities (i_{corr}) determined by curve fitting. The incorporation of D-MMT-1 filler significantly reduced the i_{corr} value from 0.15 mA/cm² to 0.023 mA/cm².

These collective findings indicate the strong corrosion protection efficacy of D-MMT filler. As shown in the schematic diagram of Fig. 9, the protective mechanism is mainly attributed to two synergistic effects: (1) Upon corrosion initiation of the Q235 steel substrate, gallic acid moieties within D-MMT react with corrosion products at the metal surface, forming a passivation film; (2) Simultaneously, as an insulating material, MMT deposits and accumulates on the substrate surface, effectively acting as a barrier to block the contact between the corrosive medium and the metal surface, as evidenced by the increased impedance. These combined actions lead to the observed enhancement in overall impedance modulus and polarization resistance (R_{ct}), thereby

significantly inhibiting the corrosion process [36]. Consequently, samples doped with D-MMT exhibit remarkably improved corrosion resistance.

3.5.2. Evaluation of corrosion resistance in diverse composite coatings

EIS is a non-destructive and sensitive technique for evaluating the dynamic corrosion protection behavior of organic coating/metal systems, as it can quantify the evolution of barrier properties, defect formation, and interfacial electrochemical reactions during prolonged exposure to corrosive media. In this study, Nyquist plots, Bode magnitude plots, and Bode phase angle plots were systematically analyzed to elucidate the effect of D-MMT loading (D-MMT-1 was taken as example) on the corrosion resistance of AL-based composite coatings over 35 days of immersion in a simulated corrosive environment (3.5 wt% NaCl solution), with pristine AL coating as the reference.

a. Nyquist Plot Analysis: Evolution of Coating Barrier Integrity

Nyquist plots (representing the relationship between the real part of impedance, Z' , and the imaginary part, $-Z''$) provide intuitive insights into the electrochemical processes at the coating/metal interface, where the radius of the capacitive reactance arc directly correlates with coating resistance (R_c)—a key parameter reflecting the coating's ability to block the penetration of corrosive species (e.g., H_2O , Cl^-).

At the initial immersion stage (day 1), all coatings (pristine AL, D-MMT-1/AL-2 %, D-MMT-1/AL-4 %, D-MMT-1/AL-6 %, D-MMT-1/AL-8 %) exhibited a single, well-defined capacitive arc with high impedance magnitudes ($Z' > 10^8\Omega\text{cm}^2$), as shown in Fig. 10(a). This phenomenon indicates that the coating matrices remained structurally intact, with no detectable penetration of corrosive media to the metal substrate interface. Correspondingly, the R_c values of all coatings were initially high (pristine AL: $\sim 1.1 \times 10^8\Omega\text{cm}^2$; D-MMT-1/AL-4 %: $\sim 6.2 \times 10^8\Omega\text{cm}^2$), while the coating capacitance (C_c) was low ($< 10^{-10}\text{ F}\cdot\text{cm}^{-2}$)—a characteristic of dense, low-defect coating structures that effectively inhibit the transport of electrolytes. Notably, D-MMT-doped coatings showed slightly larger arc radii than the pristine AL coating, which can be attributed to the “microvoid sealing effect” of D-MMT: the layered silicate platelets of D-MMT fill the nascent micropores (formed during coating curing) in the AL matrix, reducing the number of initial diffusion channels for corrosive species.

With prolonged immersion to 14 days, a progressive diminishment of the capacitive arc radii was observed for all coatings, accompanied by a 1–2 order-of-magnitude decrease in R_c and a concurrent increase in C_c (Fig. 10(a)). For the pristine AL coating, R_c dropped to $\sim 7.8 \times 10^6\Omega\text{cm}^2$, and C_c increased to $\sim 3.5 \times 10^{-9}\text{ F}\cdot\text{cm}^{-2}$, this trend is associated with electrolyte-induced swelling of the AL matrix, which promotes the

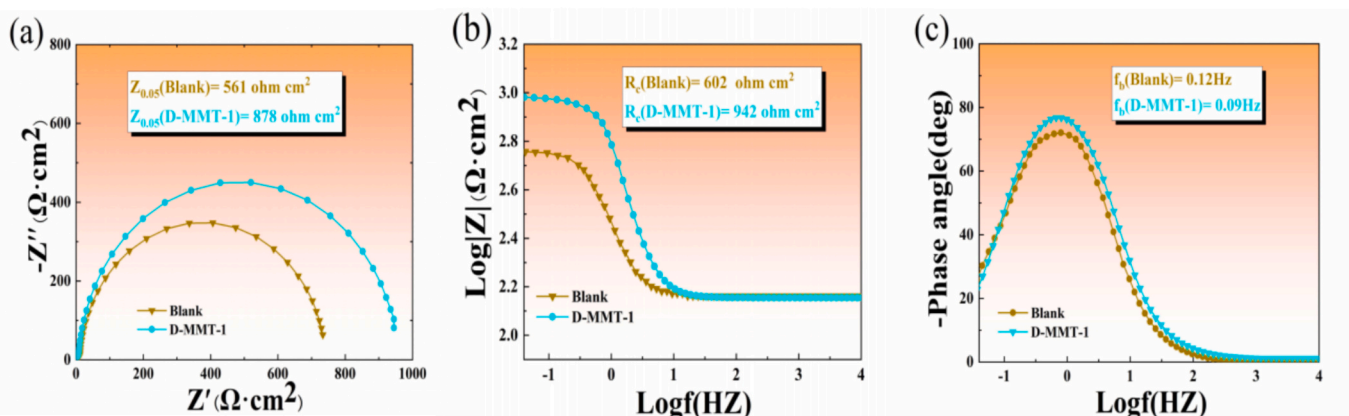


Fig. 7. (a) Nyquist plots, (b) Bode magnitude plots, and (c) phase angle plots of two Q235 steels immersed in different corrosive media (one containing D-MMT-1 and the other without) for 24 h.

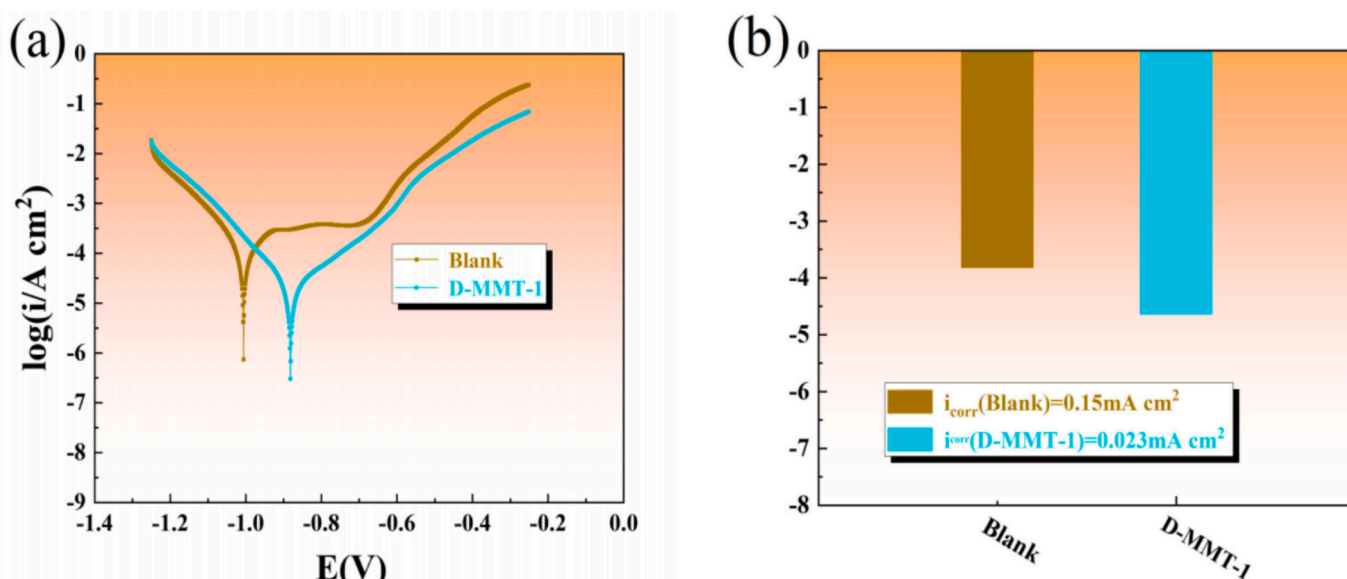


Fig. 8. (a) Polarization curves and (b) comparison of corrosion current densities of two Q235 steel plates after 24 h immersion in 3.5 wt% NaCl solution with and without D/MMT-1, respectively.

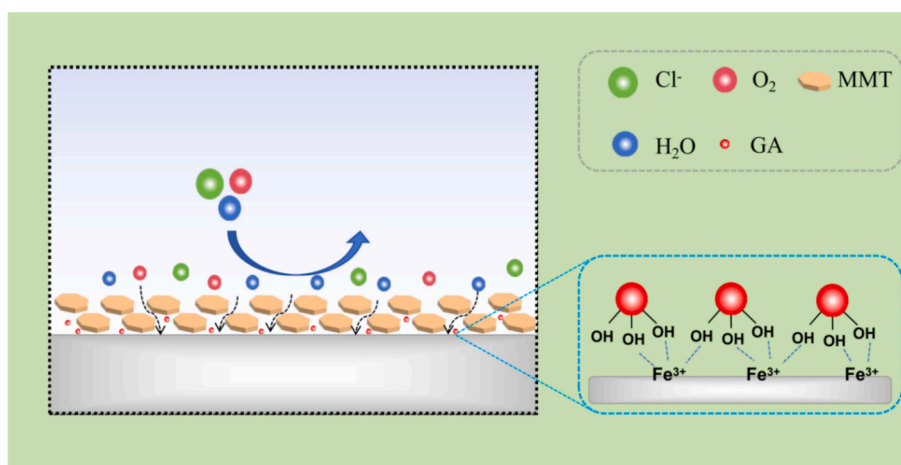


Fig. 9. Schematic diagram of the corrosion inhibition mechanism of D-MMT.

propagation of microdefects (e.g., micropores expanding to $\sim 45 \text{ nm}$, inferred from EIS equivalent circuit fitting and accelerates the penetration of corrosive media. In contrast, D-MMT-doped coatings maintained larger arc radii, with the D-MMT-1/AL-4 % coating exhibiting the smallest decline in R_c (to $\sim 1.3 \times 10^8 \Omega \cdot \text{cm}^2$). This superior mid-term stability is attributed to the “labyrinth effect” of D-MMT: the layered silicate platelets dispersed in the AL matrix form a tortuous path for corrosive species, extending their diffusion distance and slowing down penetration kinetics by a factor of ~ 12 compared to the pristine AL coating. It is worth noting that D-MMT-1/AL-6 % and D-MMT-1/AL-8 % coatings showed slightly smaller arc radii than the 4 % loading, which is likely due to the agglomeration of D-MMT particles at higher loadings. Agglomerates act as localized defect sites, creating interconnected pathways for electrolyte penetration and offsetting the barrier effect of D-MMT.

After 35 days of long-term immersion, the pristine AL coating exhibited a severely contracted capacitive arc, with its real impedance component (Z') decreasing to only $\sim 10^4 \Omega \cdot \text{cm}^2$ (Fig. 10(a)). This dramatic decline indicates that the corrosive electrolyte had completely breached the coating, reaching the underlying metal interface and

initiating localized corrosion reactions (e.g., anodic dissolution of Fe: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$, followed by the formation of rust products such as $\text{FeO}(\text{OH})$ and $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). Correspondingly, the R_c of the pristine AL coating plummeted to $\sim 4.9 \times 10^3 \Omega \cdot \text{cm}^2$, and C_c rose to $\sim 1.9 \times 10^{-6} \text{ F} \cdot \text{cm}^{-2}$, clear evidence of complete barrier failure. In stark contrast, all D-MMT-doped coatings retained significantly larger capacitive arcs, with their impedance moduli remaining within the 10^6 – $10^8 \Omega \cdot \text{cm}^2$ range. Among these, the D-MMT-1/AL-4 % coating showed the highest impedance ($Z' \approx 2.5 \times 10^8 \Omega \cdot \text{cm}^2$) and R_c ($\sim 2.1 \times 10^8 \Omega \cdot \text{cm}^2$), demonstrating exceptional long-term corrosion protection. This performance advantage arises from two synergistic effects of D-MMT: (1) the persistent “labyrinth effect” that continues to delay electrolyte penetration, and (2) the ion adsorption capacity of D-MMT—its negatively charged silicate layers selectively bind Cl^- ions, reducing the concentration of corrosive anions at the coating/metal interface and inhibiting the anodic corrosion process.

b. Bode Magnitude Plot Analysis: Quantitative Evaluation of Long-Term Protection

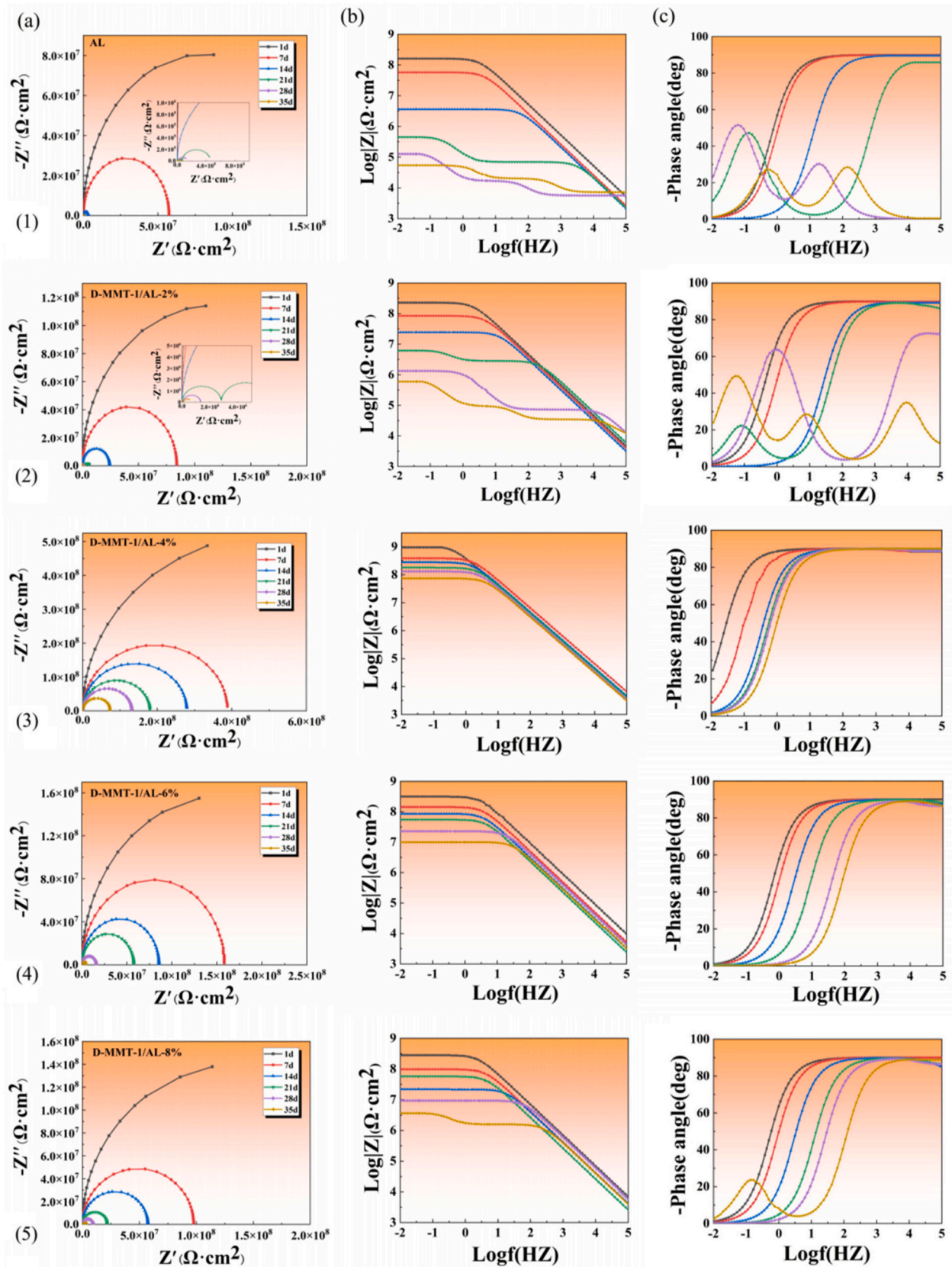


Fig. 10. Evolution of Electrochemical Impedance Behavior for D-MMT-1/AL Composite Coatings during Prolonged Corrosion Exposure. (1) Unmodified AL coating; (2) D-MMT-1/AL-2 %; (3) D-MMT-1/AL-4 %; (4) D-MMT-1/AL-6 %; (5) D-MMT-1/AL-4 % after immersion for 1–35 days. (a) Nyquist, (b) Bode magnitude, (c) Bode phase angle representations.

Bode magnitude plots are critical for quantifying the long-term corrosion protection capability of coatings, especially at the low-frequency region (0.01 Hz)—a frequency corresponding to the mass transport process of corrosive species at the coating/metal interface, and thus a reliable indicator of long-term barrier performance.

At the initial testing stage (day 1), the impedance modulus of the D-MMT-1/AL-4 % coating at 0.01 Hz reached $\sim 10^9 \Omega \cdot \text{cm}^2$, which is 5–10 times higher than that of the pristine AL coating ($\sim 1.6 \times 10^8 \Omega \cdot \text{cm}^2$) and other D-MMT loadings (D-MMT-1/AL-2 %: $\sim 3.4 \times 10^8 \Omega \cdot \text{cm}^2$; D-MMT-1/AL-6 %: $\sim 7.1 \times 10^8 \Omega \cdot \text{cm}^2$; D-MMT-1/AL-8 %: $\sim 5.3 \times 10^8 \Omega \cdot \text{cm}^2$), as shown in Fig. 10(b). This significant difference confirms that the 4 wt% D-MMT loading optimizes the balance between matrix compatibility and barrier effect: lower loadings (2 %) provide insufficient layered platelets to form an effective “labyrinth” structure, while higher loadings (6 %, 8 %) may lead to particle agglomeration that creates microdefects and weakens the barrier performance.

During the 35-day immersion experiment, the D-MMT-1/AL-4 % coating exhibited a slow and gradual decline in $|Z|$ at 0.01 Hz, decreasing from $\sim 10^9 \Omega \cdot \text{cm}^2$ to $\sim 10^8 \Omega \cdot \text{cm}^2$ (Fig. 10(b), curve 5). This slow decay trend is indicative of a dense cross-linked structure and corrosion inhibition effect of corrosion inhibitor (Gallic acid) in coatings, which effectively prevents coating swelling (a major cause of matrix degradation) and interfacial delamination (a key pathway for electrolyte infiltration). In contrast, the pristine AL coating showed a “cliff-like” decline in $|Z|$ at 0.01 Hz, dropping from $\sim 1.6 \times 10^8 \Omega \cdot \text{cm}^2$ to $\sim 10^4 \Omega \cdot \text{cm}^2$ —an attenuation amplitude exceeding 4 orders of magnitude. This rapid degradation is attributed to the loose structure of the pristine AL coating, which allows corrosive media to quickly penetrate through interconnected micropores and reach the metal substrate. Additionally, the Bode magnitude curve of the pristine AL coating after 35 days lacks the characteristic low-frequency plateau, further confirming the loss of barrier function and the direct exposure of the metal substrate to the electrolyte.

c. Phase Angle Plot Analysis: Insight into Coating Capacitive Behavior and Ion Diffusion

Phase angle plots (depicting the relationship between phase angle, θ , and frequency) reflect the electrochemical nature of the coating/metal system, where the width of the near -90° phase angle plateau is positively correlated with coating compactness: a broader plateau indicates fewer microdefects, stronger capacitive behavior, and thus better barrier performance.

At the initial immersion stage, all coatings exhibited wide near -90° phase angle plateaus (Fig. 10(c)), confirming their effective initial capacitive behavior and barrier function. The D-MMT-1/AL-4 % coating showed the widest plateau, spanning a frequency range of 10^0 – 10^4 Hz—wider than that of the pristine AL coating (10^2 – 10^4 Hz)—which is consistent with its denser structure and fewer initial defects. With increasing immersion time, the frequency-dependent evolution of phase angle differed significantly between the pristine AL coating and D-MMT-doped coatings:

High-frequency region ($>10^3$ Hz): Both the pristine AL coating and D-MMT-doped coatings maintained phase angles near -90° , reflecting dominant double-layer capacitive behavior at the coating/electrolyte interface. This indicates that the outer surface of all coatings remained intact, with no significant adsorption of corrosive species on the surface.

Mid-frequency region (10^0 – 10^3 Hz): The pristine AL coating exhibited a sharp transition in phase angle from -90° to $\sim -45^\circ$, which is associated with significant charge transfer (CT) processes at the coating/metal interface. This transition arises from the synergistic effect of charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}), as the electrolyte penetrates the coating and initiates electrochemical reactions at the metal surface. In contrast, D-MMT-doped coatings (especially the 4 % loading) showed a gentler phase angle transition, with values stabilizing at $-60^\circ \sim -45^\circ$. This difference is attributed to the

ability of D-MMT to suppress ion migration: the layered silicate platelets block the transport of ions (e.g., Cl^- , Fe^{2+}) and retard electrochemical kinetics, increasing R_{ct} by ~ 3 orders of magnitude (from $\sim 10^4 \Omega \cdot \text{cm}^2$ for the pristine AL coating to $\sim 10^7 \Omega \cdot \text{cm}^2$ for the D-MMT-1/AL-4 % coating, calculated via equivalent circuit fitting with the $R(Q(R(QR)))$ model).

Low-frequency region ($<10^0$ Hz): The pristine AL coating showed a phase angle approaching 0° with a flat curve, indicating pure resistive behavior—this means the coating has completely lost its capacitive characteristics, and the metal substrate is directly exposed to the electrolyte. In this case, Warburg impedance (Z_w , associated with ion diffusion) is negligible due to unimpeded diffusion of corrosive species, leading to accelerated corrosion. For the D-MMT-1/AL-4 % coating, the phase angle remained above -45° with a flattened plateau, confirming limited ion diffusion: the layered structure of D-MMT prolongs the diffusion path of corrosive media, preventing direct contact between the electrolyte and the metal substrate and maintaining the coating's capacitive behavior.

Fig. 11 presents the Tafel polarization curves of composite coatings with different D-MMT loadings after 35 days of immersion in a 3.5 wt% NaCl solution. The variations in the slopes of the anodic and cathodic branches reveal the inhibition mechanism of the coatings against corrosion. As shown in Table S1, the corrosion current density (i_{corr}) reached its minimum value of $2.343 \times 10^{-9} \text{ A/cm}^2$ at 4 wt% D-MMT-1, which is two orders of magnitude lower than that of the pure AL coating ($2.307 \times 10^{-7} \text{ A/cm}^2$) (Table S1). Notably, quantitative analysis of the Tafel slopes provides deeper insights into the corrosion kinetics. All composite coatings exhibited higher cathodic Tafel slopes (β_c) compared to the pure AL coating. At 4 wt% D-MMT-1 loading, β_c increased to 522.34 mV/dec, indicating a significantly enhanced activation energy barrier for the cathodic oxygen reduction reaction (ORR). This change can be attributed to: (1) the physical barrier effect, where MMT nano-sheets prolong the diffusion path of O_2 (labyrinth effect); and (2) the chemical passivation effect, wherein gallic acid (GA) migrates to defective areas and chelates dissolved oxygen via its phenolic hydroxyl groups, reducing the O_2 concentration at cathodic sites [40]. Meanwhile, the anodic Tafel slope (β_a) of the 4 wt% D-MMT-1 coating ($\sim 297.25 \text{ mV/dec}$) increased by 30.8 % compared to that of the pure AL coating ($\sim 95.12 \text{ mV/dec}$, Table S1), demonstrating strong suppression of the anodic metal dissolution reaction. This is due to: (1) Fe^{2+} chelation and passivation, where GA forms a dense organic-inorganic hybrid layer with corrosion-induced Fe^{2+} , blocking anodic active sites; and (2) defect repair, wherein GA reduces Fe^{3+} to stable Fe^{2+} -catechol complexes, sealing micro-pores. For all the composite coatings, the ratio of β_c to β_a approaches the theoretical optimal value of 2.0, indicating balanced suppression of both anodic and cathodic reactions (mixed control mechanism). However, when the D-MMT-1 loading increased to 8 wt%, β_c and β_a decreased to 259.25 mV/dec and 131.65 mV/dec, respectively, leading to: (1) weakened cathodic control (decreased β_c) due to MMT agglomerates disrupting the coating integrity and accelerating O_2 diffusion; (2) accelerated anodic reaction (decreased β_a) as exposed active metals at interfacial defects promote localized dissolution; and (3) an increase in corrosion current density to $5.192 \times 10^{-9} \text{ A/cm}^2$, validating the “defect-dominated failure” model [38].

3.5.3. Microscopic analysis of surface morphology and chemical composition changes at coating scratches after corrosion

To further confirm the effective participation of GA in D-MMT in chelating metal corrosion products, scratches were deliberately introduced on both plain AL coatings and D-MMT/AL-4 % coatings. These scratched samples were then immersed in a saline solution (3.5 wt% NaCl) for 35 days. The scratch regions were subsequently characterized using FE-SEM and XPS analyses to probe the interfacial morphology and surface chemical composition, respectively..

Fig. 12a shows the FESEM image of a damaged region on a standard AL coating. Severe corrosion is observed at the scratched site, with the groove densely filled with rust. EDS analysis of this area confirmed

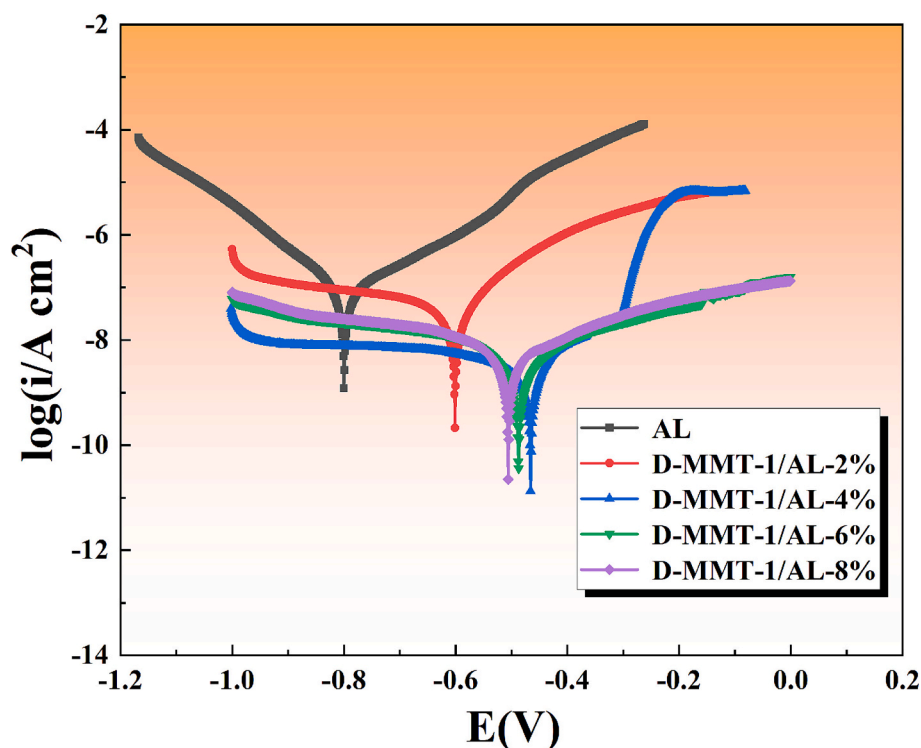


Fig. 11. Polarization curves of the modified coatings after being immersed in corrosive media for 35 days.

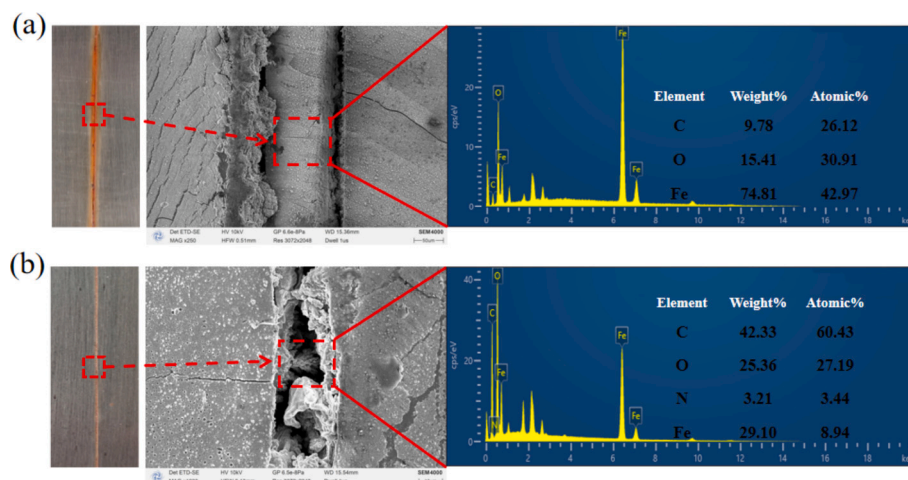


Fig. 12. FESEM images and corresponding EDS analysis of scratch regions on coatings after 35-day immersion in saline solution: (a) AL coating; (b) D-MMT-1/AL-4 % composite coating.

significant iron corrosion, revealing an exceptionally high iron mass percentage of 74.81 % within the scanned region. In contrast, Fig. 12b presents the morphology of a damaged area on the D-MMT/AL-4 % coating. The corresponding EDS analysis revealed a significantly reduced iron mass percentage of 29.9 % at the damaged site. Notably, this location exhibited elevated levels of carbon (C) and oxygen (O), along with a trace amount of nitrogen (N).

This distinct elemental composition arises because although corrosion occurs at the exposed metal substrate upon damage and immersion in saline solution, GA incorporated within the composite coating demonstrates high mobility in the aqueous phase [37]. The mobilized GA migrates to the scratch site, where it reacts with ferrous ions generated by the corrosion process, forming insoluble GA-iron chelate complexes. Collectively, these results demonstrate that the D-MMT

doped composite coating exhibits an effective rust conversion capability.

To investigate the changes in surface elements of different coatings during the corrosion process and thereby deduce their anti-corrosion protection mechanisms, XPS analysis was performed on the exposed iron plate surfaces at the scratched areas of AL coating and D-MMT-1/AL-4 % composite coating after being immersed in a 3.5 wt% NaCl solution for 35 days.

As illustrated in Fig. 13a, the O_{1s} spectra of both coatings exhibit distinct peak positions and shapes. For the AL coating, the main peak at approximately 531.5 eV is typically assigned to C=O/C-O functional groups in polymer coatings. In contrast, the D-MMT-1/AL-4 % composite coating shows a main peak shift to a lower binding energy of ~530.8 eV, accompanied by a shoulder peak. This shift of binding

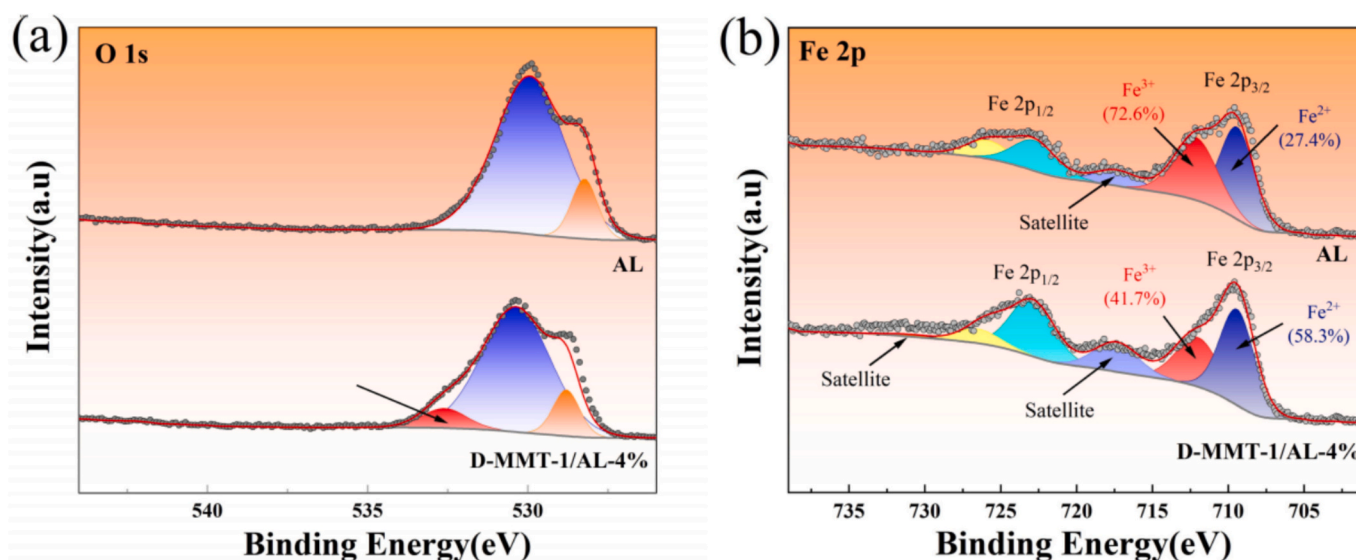


Fig. 13. XPS analyses of the scratch regions on coatings after 35-day immersion in saline solution: (a) AL coatings; (b) D-MMT-1/AL-4 % composite coating.

energy indicates an altered chemical environment of oxygen atoms, likely due to the change of coordination between oxygen-containing functional groups (e.g., catechol/carboxyl groups in gallic acid) and metal ions (i.e., chelation with iron ions). Deconvolution of peaks further reveals changes in the ratio of hydroxyl/adsorbed water, corroborating the existence of interfacial reactions. Fig. 13b compares the transitions of iron valence states in control and experimental coatings. For the conventional AL-cured coating, corrosion products of iron are predominantly Fe³⁺ (72.6 %), consistent with typical chemical states of iron oxides/hydroxides (e.g., α -Fe₂O₃, FeOOH). In contrast, the D-MMT-1/AL-4 % composite coating exhibits a significant valence shift: the Fe²⁺ fraction increases to 58.3 %, while Fe³⁺ decreases to 41.7 %. This reduction of Fe³⁺ to Fe²⁺ is promoted by active components in D-MMT, likely due to the strong reducing and chelating capabilities of gallic acid. Such intervention effectively alters the transformation pathway of metallic corrosion products. Additionally, the chelated complex demonstrates enhanced structural stability and a more delocalized electron distribution, potentially narrowing the FWHM (full width at half maximum) of Fe_{2p} characteristic peaks.

The enrichment of Fe²⁺ at scratch regions of the D-MMT-1/AL-4 % composite coating, coupled with corrosion inhibition observed through FESEM, demonstrates a tripartite corrosion inhibition mechanism: (i) Gallic acid mediates dual chelation-reduction reactions, converting corrosive Fe³⁺ species into stable Fe²⁺ complexes; (ii) The resulted dense Fe²⁺-organic chelate layer physically blocks active corrosion sites, reducing ionic permeability by two orders of magnitude; (iii) Passivation of the metal/coating interface via electron delocalization within the chelate structure constitutes the core mechanism for enhanced corrosion resistance [38–40].

Lastly, it is necessary to discuss and elaborate on the comparison of the actual anti-corrosion capability of the composite coatings fabricated with different proportions.

For the D-MMT-1/AL-4 % coating, GA is initially uniformly dispersed within the coating matrix (FESEM-EDS analysis reveals uniform distribution of C and O elements). Polarization drives the rapid migration of GA toward the coating/electrolyte interface or minor internal defects. In the short term, a dense passive film forms via the chelation of Fe²⁺ and reduction of Fe³⁺, resulting in enhanced initial corrosion resistance (characterized by low corrosion current density and high impedance). Following long-term polarization, however, local GA depletion occurs in the coating due to sustained migration: the passive film at the interface lacks continuous GA supplementation and thus fails to resist Cl[−] attack, leading to passive film rupture (i.e., the onset of “breakdown potential”).

In contrast, the D-MMT-1/AL-6 % and D-MMT-1/AL-8 % coatings contain a higher total GA content. Even when migration occurs, sufficient GA remains within the coating to maintain passive film stability, thereby yielding superior electrochemical performance after breakdown.

X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) analyses confirm that D-MMT-1/AL-4 % represents the optimal dispersion ratio (interlayer spacing: 1.680 nm; no obvious agglomeration). The “labyrinth effect” generated by this dispersion maximizes physical barrier capacity, which is the primary contributor to the excellent initial corrosion resistance. Nevertheless, this highly dispersed interface structure exhibits a “stability limitation” under polarization conditions: In the D-MMT-1/AL-4 % coating, the hydrogen-bonding interactions between the resin and D-MMT are susceptible to dynamic reorganization under continuous applied potential. This reorganization induces the formation of interfacial microcracks between some nanosheets and the resin matrix; these microcracks act as rapid penetration pathways for Cl[−] and H₂O, accelerating coating breakdown. Although minor D-MMT agglomeration is observed in the cross-sectional morphologies of D-MMT-1/AL-6 % and D-MMT-1/AL-8 % coatings (see Fig.S4), the “locally dense regions” formed between agglomerates and the resin provide structural support under polarization, mitigating the formation and propagation of interfacial microcracks. While the agglomerates themselves reduce initial barrier properties (resulting in slightly lower initial corrosion resistance than the 4 wt% coating), the synergistic effect of “physical support + residual GA passivation” maintains superior electrochemical behavior after breakdown.

4. Conclusion

This study successfully developed a multifunctional anti-corrosion coating by integrating gallic acid (GA)-modified montmorillonite (D-MMT) into an AL matrix. The D-MMT nanofiller, synthesized via ion-exchange of *N,N*-dimethylstearylamine gallate (DMSAG), exhibited expanded interlayer spacing (from 1.270 nm to 1.680 nm) and homogeneous dispersion within the polymer, as confirmed by XRD and FESEM. At the optimal 4 wt% loading (D-MMT-1/AL-4 %), the composite coating present superior performance such as enhanced mechanical properties and exceptional corrosion protection. The increased hardness (from B to HB), superior wear resistance (minimal mass loss rate), and improved thermal stability (decomposition temperature increased 20 °C, from 360 to 380 °C) are due to the hydrogen bonding between nanofillers and resin. The exceptional corrosion protection has

been evidenced by the fact of the low-frequency impedance modulus reached $10^8 \Omega \cdot \text{cm}^2$ —two orders higher than pure AL coatings—while corrosion current density decreased from 2.307×10^{-7} to 2.343×10^{-9} A/cm², after 35-day immersion in 3.5 wt% NaCl.

The post-damage interface passivation protection mechanism was discussed as that GA-mediated chelation-reduction converted corrosive Fe³⁺ to stable Fe²⁺-chelate complexes (58.3 % Fe²⁺ enrichment at scratches), forming a dense passivation layer that blocked active sites. FESEM-EDS validated reduced iron content (29.9 % vs. 74.81 % in AL) and elemental redistribution at damaged regions.

Based on a corrosion current density reduction of >50 % and an impedance modulus increase of >100×, the composite coating is capable of extending the service life of marine infrastructure by 3–5 years. Given that global annual corrosion costs exceed 1 trillion USD, this coating could yield annual savings of 110 billion USD in maintenance and replacement expenses. Additionally, compared with chromate-based systems, the adoption of low-cost natural inhibitors achieves a 30 % cost reduction—an advantage that enhances scalability for industrial applications such as offshore platforms and ship hulls.

CRedit authorship contribution statement

Ruofei Liu: Investigation. **Xiao Wang:** Resources. **Jinbiao Wang:** Data curation. **Zhe Lin:** Methodology, Software. **Lizhuang Chen:** Software. **Zhaolei Li:** Validation. **Zhengbai Zhao:** Visualization. **Hui Yan:** Writing – review & editing. **Lixin Xu:** Methodology, Project administration. **Weili Li:** Supervision, Writing – original draft.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2025.109649>.

Data availability

Data will be made available on request.

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