

Advanced bio-inspired urushiol-modified SiO₂@BN hybrids for enhanced thermal conductivity and superior corrosion resistance in waterborne epoxy coatings

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ABSTRACT

This study developed an urushiol-based bio-inspired composite coating incorporating synergistic SiO₂@BN hybrids to achieve high thermal conductivity and superior corrosion resistance. Conventional resin coatings (e.g., epoxy, polyurethane) exhibit excellent barrier properties but suffer from low thermal conductivity (<0.2 W/(m·K)), limiting heat dissipation and promoting corrosion under thermal cycling. To address this, hexagonal boron nitride (h-BN) was modified via a sol-gel process with a silica (SiO₂) layer, followed by functionalization with methacryloxypropyl trimethoxysilane (MPS) and grafting with natural urushiol (Ur) to form a hydrophobic and highly dispersible hybrid filler (USB). The USB filler was incorporated into a waterborne epoxy (WEP) matrix at various loadings (0.5–2.0 wt%). The optimal composite coating (USB/WEP-1.5 %) demonstrated a thermal conductivity of 0.4712 W/(m·K) (86 % improvement over pure WEP), excellent mechanical properties, and outstanding corrosion resistance with a low-frequency impedance modulus of $2.33 \times 10^{10} \Omega \cdot \text{cm}^2$ after 270 h immersion in 3.5 % NaCl. The enhancement is attributed to the synergistic effect of urushiol's catechol groups and long alkyl chains, which improve dispersion, interfacial compatibility, and electrochemical passivation.

1. Introduction

Advancing technology and expanding market demands are steadily increasing the need for coatings in specific applications. Beyond environmental performance, functional requirements for coatings are becoming increasingly prominent, as standalone anti-corrosion properties can no longer adequately meet practical application needs. Multi-functional integration has emerged as a critical direction in coating design, incorporating properties such as thermal conductivity, optical functionality, and acoustic performance, which represent new trends in contemporary coating development. For instance, in high-temperature environments (such as desalination applications), chloride ions in corrosive conditions can trigger pitting and crevice corrosion, potentially leading to localized perforations in metal protective layers.

Simultaneously, if a coating reduces the heat dissipation capacity of metals, it can significantly accelerate corrosion rates and may even induce failure modes such as stress corrosion cracking [1–4]. Consequently, developing protective coatings that combine excellent corrosion resistance with high thermal conductivity is essential for enhancing equipment longevity and energy efficiency. An ideal coating must effectively block corrosive media such as H₂O, Cl[−], and O₂, while maintaining high thermal conductivity to minimize additional thermal resistance and prevent a reduction in heat transfer efficiency [5–10].

Although conventional resin coatings—such as acrylic, epoxy, and polyurethane—demonstrate excellent barrier properties and strong adhesion, their inherently low thermal conductivity (typically below 0.2 W/(m·K)) considerably restricts efficient heat dissipation. In practical service environments, these materials function as thermal

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insulation layers, thereby diminishing energy efficiency. Furthermore, under repeated thermal cycling and mechanical stress, resin matrices are susceptible to degradation, leading to microcracking and interfacial delamination. These defects facilitate the infiltration of corrosive agents and may accelerate localized corrosion. A widely adopted approach to improve the thermal conductivity of polymeric coatings involves the incorporation of highly conductive inorganic nanofillers. Among these, hexagonal boron nitride (h-BN) is regarded as an ideal candidate owing to its layered structure, high thermal conductivity, and electrical insulation properties. However, BN nanosheets exhibit an inherent tendency to agglomerate, resulting in poor dispersion, interfacial defects, and ultimately, compromised protective performance due to enhanced permeability to corrosive species [11–16]. To overcome the dispersion limitations of BN, surface modification strategies are frequently employed to enhance compatibility with the polymer matrix. For instance, Kang et al. [16] implemented a surface charge modulation strategy by grafting charged functional groups (e.g., pyrrolidinium salts) onto BN, thereby strengthening electrostatic repulsion and improving dispersion stability. Alternatively, Hanif et al. [17] developed a non-covalent functionalization approach through the deposition of plant-derived tannic acid (TA) onto BN nanotubes (BNNs), followed by the incorporation of decylamine (DA), significantly enhancing the dispersibility of BN within resin-based systems.

Polydopamine (PDA), a mussel-inspired polymer, is widely used as a versatile surface modifier for inorganic fillers. Its catechol and amine groups enable robust interfacial bonding with materials such as boron nitride (BN), enhancing filler dispersion in polymer matrices. Researchers have developed various PDA-based nanocontainers for corrosion protection: Chen et al. [18] constructed GO@PBH by coating BTA-loaded HNTs with a pH-responsive PDA layer and assembling with GO via π - π stacking; Wang et al. [19] prepared BPB using PDA-modified BNNs loaded with BTA, achieving triple functions of high loading, pH-responsive release, anticorrosion, and UV shielding; Xu et al. [20] fabricated PDA-PEI@HMCM-BTA by encapsulating hollow mesoporous CeO_2 —serving as both a $\text{Ce}^{3+}/^{4+}$ source and BTA carrier—with a PDA/PEI hybrid layer for synergistic inhibition. Despite these advantages, PDA has limitations: high precursor cost hinders large-scale use, and its inherent hydrophilicity may increase coating water uptake, compromising long-term anticorrosion performance [21–23].

In contrast, Urushiol (Ur), a bio-based molecule from natural lacquer, contains catechol groups that provide strong adhesion and reducibility comparable to polydopamine (PDA). Its C15–C17 long alkyl chains impart marked hydrophobicity and improved compatibility with organic resins. Studies show urushiol forms dense, stable modification layers on material surfaces, enhancing composite mechanical properties, thermal stability, and corrosion resistance [24–28], making it a promising candidate for BN surface modification.

Existing modification methods, however, often target single functionalities. Sun et al. [29] modified BN nanosheets (BNNs) with urushiol to enhance hydrophobicity and anticorrosion, but interfacial binding relied mainly on physical adsorption, limiting long-term stability. Li et al. [30] co-modified BNNs with SiO_2 and a silane coupling agent, improving dispersion, thermal conductivity, and mechanical properties, yet the coating lacked active corrosion inhibition.

To address these limitations, this study introduces a novel three-step sequential modification strategy to fabricate a multifunctional epoxy composite coating integrating high thermal conductivity, superior corrosion resistance, and excellent mechanical properties. The strategy involves: (1) constructing a silica layer on BN via sol-gel TEOS to enhance reactivity and thermal stability; (2) modifying with MPS to introduce C=C bonds; and (3) grafting urushiol via self-polymerization and coupling, yielding a hydrophobic, interface-compatible hybrid Ur-SiO_2 @BN (USB).

This core-shell structure offers key advantages: robust “BN–O–Si–O–Si–(urushiol)” covalent bonding ensuring interfacial stability; synergistic dispersion from SiO_2 steric hindrance and urushiol

hydrophobic compatibility; and multifunctional integration— SiO_2 /silane enhancing thermal and mechanical performance, while urushiol provides active corrosion inhibition and hydrophobicity.

This work systematically examines USB dispersion in waterborne epoxy, corrosion protection mechanisms, and coating thermal conductivity, offering material design insights and theoretical support for high-performance coatings suited to harsh environments such as seawater desalination systems.

1.1. Materials

Stacked hexagonal boron nitride (h-BN), characterized by its layered structure and a large size distribution of 10–15 μm , was provided by Shanghai Mclin Biochemical Technology Co., Ltd. Urushiol was bought from Wuhan Lullaby Pharmaceutical & Chemical Co., Ltd. Epoxy resin (DER331) was acquired from Dow Chemicals Co., Ltd. The epoxy emulsifier Reactsurf 0092 was sourced from Solvay Chemicals Co., Ltd. An aqueous polyamide curing agent (AQUAEPO-3132) was procured from Jiangsu Fuqisen New Materials Co., Ltd. Propylene glycol methyl ether (PM), used as a cosolvent, was purchased from Tianjin Zhonghe Shengtai Chemical Co., Ltd. Wetting dispersant (YCK-2601), leveling agent (YCK-1110), and defoaming agent (YCK-810) were generously supplied by Shanghai ICKE Chemical Technology Co., Ltd.

1.2. Fabrication of silica-coated boron nitride (SiO_2 @BN) composite

Hexagonal boron nitride (h-BN) was doped in a blended solvent consisting of anhydrous ethanol and deionized water. The mixture was ultrasonicated at room temperature for 30 min to ensure thorough dispersion. The resulting suspension was then transferred to a constant-temperature water bath, followed by the addition of aqueous ammonia to adjust the pH to 9–10. The mixture was continuously stirred at 60 °C for 10 min to form a homogeneous suspension, denoted as Solution A.

TEOS, designated as Solution B, was then added dropwise into Solution A at a rate of approximately 0.1 mL/min via a constant-pressure dropping funnel while being continuously stirred. After complete addition, the reaction system was maintained at 30 °C with stirring for 6 h to allow the sol-gel reaction to proceed, facilitating the in-situ deposition and coating of silica on the h-BN surface.

Upon completion of the reaction, the product was collected via vacuum filtration with a Büchner funnel. The collected product was washed three times with anhydrous ethanol to remove residual ammonia and by-products. The solid product was then dried in a vacuum oven at 50 °C for 24 h, yielding a white powder designated as the SiO_2 @BN composite.

1.3. Fabrication of urushiol-modified SiO_2 @BN composite (USB)

SiO_2 @BN was dispersed in absolute ethanol, followed by the addition of 3-(trimethoxysilyl) propyl methacrylate (MPS). The mixture was stirred at room temperature for 24 h to ensure complete surface modification of the SiO_2 @BN particles. After being washed with ethanol and dried under vacuum at 50 °C for 24 h, MPS-modified SiO_2 @BN (referred to as MS@BN) was obtained. MS@BN was then redispersed in absolute ethanol, with subsequent addition of urushiol (Ur) and azobisisobutyronitrile (AIBN). The radical-initiated reaction was conducted at 70 °C for 12 h. Upon completion of the reaction, the product was washed with ethanol and dried under vacuum at 50 °C for 24 h to yield urushiol-modified silicon-coated boron nitride (referred to as USB).

1.4. Preparation of USB/WEP composite coatings

The waterborne epoxy dispersion (WEP) with a solid content of 60 wt % was formulated using epoxy resin DER331 as the matrix resin and waterborne epoxy emulsifier 0092, with detailed preparation procedures described in this paper [31].

The aqueous composite filler dispersion was then prepared. Following the addition of a wetting dispersant, the obtained USB was dispersed in a blended solution of propylene glycol methyl ether (PM) and H₂O. After 20 min of ultrasonic treatment, a stable aqueous dispersion of USB was achieved, which was subsequently incorporated into the waterborne epoxy (WEP) resin via mechanical stirring to ensure homogeneous dispersion. To evaluate the influence of USB loading on the composite coating properties, various mass fractions (0.5 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt%) of USB were introduced. For clarity, the resulting composite coatings are referred to as USB/WEP-X%, where X denotes the mass percentage of the filler ($X = 0.5, 1.0, 1.5$, and 2.0). For comparative purposes, a reference coating containing unmodified hexagonal boron nitride (h-BN) at 1.5 wt% was also prepared and designated as BN/WEP-1.5 %.

To investigate the cross-sectional morphology of coatings derived from the USB/WEP-X%, steel panels and silica glasses were selected as substrates. Prior to coating application, the steel substrates underwent sequential sandpaper polishing and cleaning with alcohol to remove

surface contaminants. The USB/WEP-X%, combined with the aqueous polyamide curing agent, were homogenized and uniformly applied onto the substrates using a precision wire-wound rod. Curing was conducted at 60 °C for 8 h to ensure complete crosslinking between the resin and curing agent. After curing, the coatings were conditioned at ambient temperature (25 ± 2 °C) for 168 h to achieve equilibrium prior to characterization. Using the same processing method, BN/WEP-1.5 % composites were also fabricated into coatings, serving as a comparative reference for analyzing morphology and properties.

The schematic of the preparation process for the USB and USB/WEP composite coatings is shown in Fig. 1.

1.5. Characterization

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

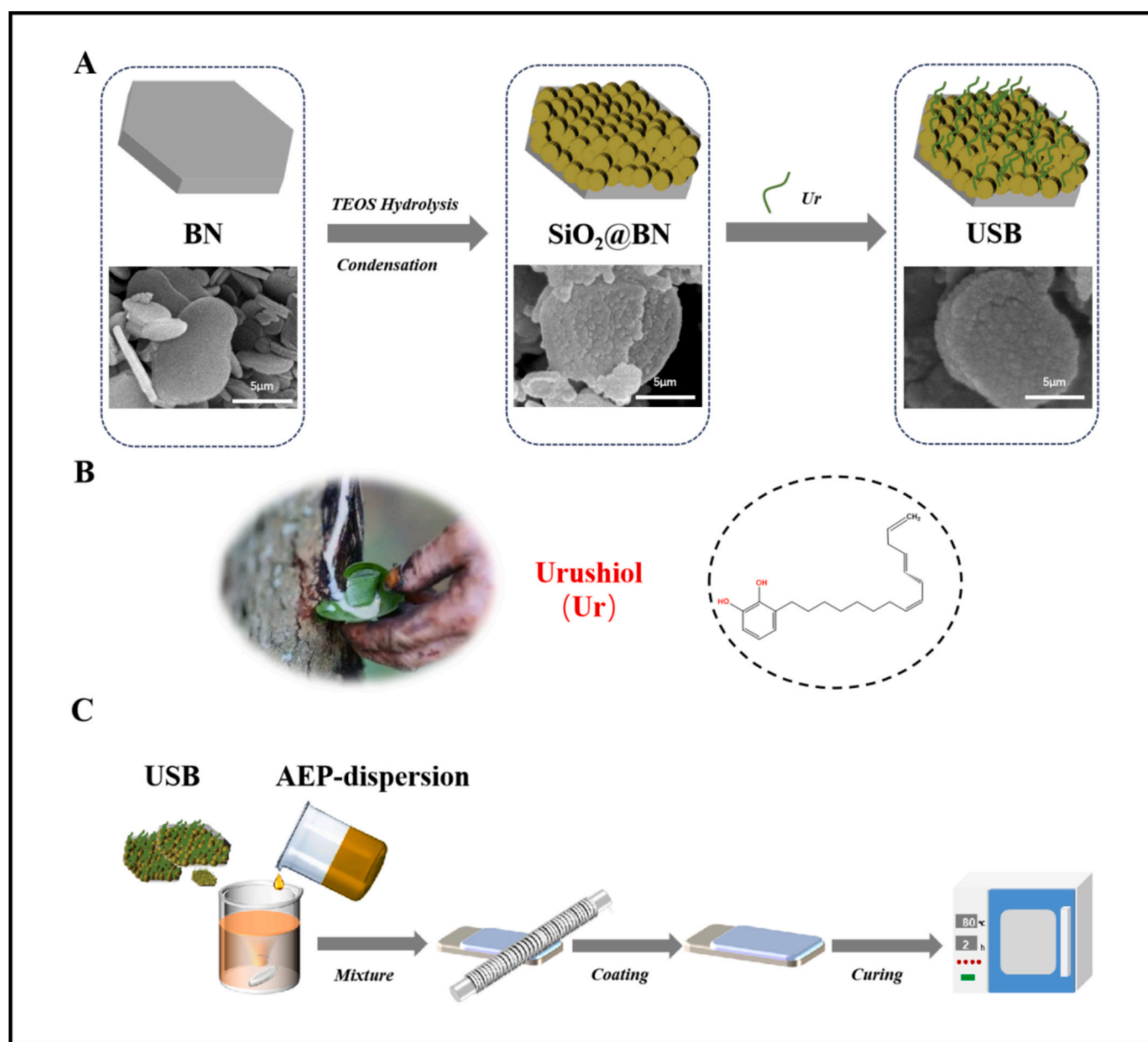


Fig. 1. (A) Schematic diagram of the brief preparation process of USB modified filler and FESEM images of BN, SiO₂@BN, and USB; (B) Urushiol is in nature, the molecular structural formula of urushiol; (C) Schematic diagram of the brief preparation process of USB/WEP composite coating.

Advance X-ray diffractometer. The Cu K α -ray ($\lambda = 0.154$ nm) was used as the energy source, with a test range of 5° to 85° and a scanning rate of $5^\circ/\text{min}$. UV–Vis spectra were recorded on an Agilent Cary 5000 UV–Vis–NIR spectrophotometer over a wavelength range of 200 to 600 nm. ^{13}C NMR spectra were acquired using a JEOL NMR spectrometer operating at [frequency, if known] MHz, with samples dissolved in an appropriate deuterated solvent. 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-EDS analyses were performed on a Hitachi S4700 (Tokyo, Japan) with a field emission gun at 13.0 kV and 25 μA . 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 a pencil, according to the GB/T 6739–2006 method. Thermal imaging of the coatings was carried out using an infrared camera from Gewu Youxin Technology. The thermal conductivity of the composite coatings was determined by measuring thermal diffusivity using a Laser Flash Analyzer (LFA 467 HyperFlash, Netzsch, Germany). Measurements were performed in the through-thickness direction. The thermal conductivity (λ , $\text{W}/(\text{m}\cdot\text{K})$) was calculated using the formula $\lambda = \alpha \times C_p \times \rho$, where α is the thermal diffusivity (mm^2/s), C_p is the specific heat capacity ($\text{J}/(\text{g}\cdot\text{K})$), and ρ is the bulk density (g/cm^3). 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 the coating, and high-resolution scanning was conducted for elements that exist 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 – 0 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 . Additionally, the EIS fits were verified by chi-squared (χ^2) values. All systems exhibited χ^2 values on the order of 10^{-4} , demonstrating excellent agreement with the equivalent circuit models and validating the fitting procedure and data reliability.

2. Results and discussion

2.1. The structure and properties of USB and its intermediates

The surface morphology and microstructure of pristine h-BN, $\text{SiO}_2@\text{BN}$, and USB composite powders were characterized by field emission scanning microscopy (FESEM), as shown in Fig. 2(A–D). Pristine h-BN displays a typical layered structure with a relatively smooth surface but tends to aggregate due to interlayer interactions. In contrast, $\text{SiO}_2@\text{BN}$ exhibits significant morphological changes: silica particles form a dense, continuous coating on the h-BN surface, nearly fully encapsulating the basal layers. The coating is tightly adhered to the substrate, and boundaries between particles become indistinct due to fusion, resulting in enhanced surface roughness and reduced agglomeration [13]. Elemental analysis further confirms the structural evolution, with significantly intensified signals of Si and O observed in $\text{SiO}_2@\text{BN}$. Meanwhile, the carbon content increases markedly in the USB composite powder, accompanied by a reduction in surface roughness. This phenomenon is attributed to the successful grafting of urushiol (Ur)-a natural organic polymer containing long alkyl chains (C_{15} – C_{17})-onto the $\text{SiO}_2@\text{BN}$ surface [26], which improves the material's dispersibility and surface properties, confirming the successful preparation of the USB composite.

To verify the successful formation of a SiO_2 coating on h-BN and the effective grafting of urushiol (Ur), a series of characterization techniques was employed, which are summarized in Fig. 3.

In Fig. 3A, the FTIR spectra of raw materials and the as-prepared USB are shown. In the spectrum of $\text{SiO}_2@\text{BN}$, absorption peaks at 458 cm^{-1} and 1081 cm^{-1} are assigned to the bending vibration and symmetric stretching vibration of Si–O–Si bonds, respectively. Peaks at 949 cm^{-1}

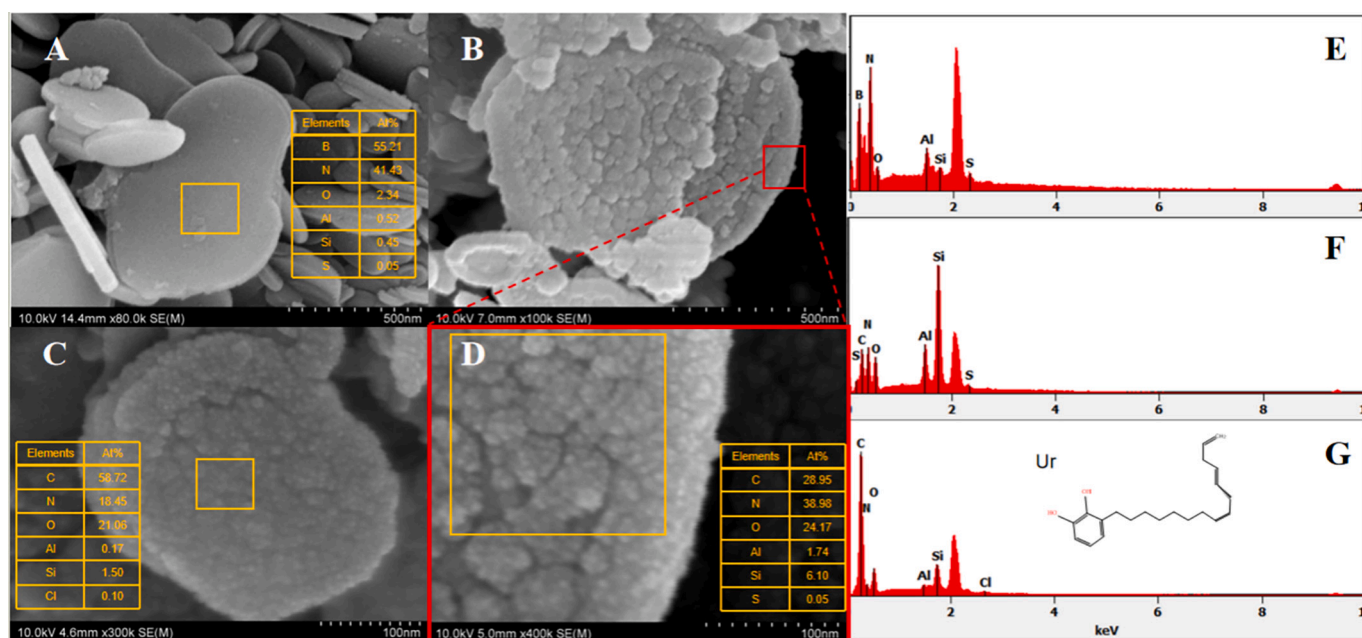


Fig. 2. FESEM photos of (A) h-BN, (B) $\text{SiO}_2@\text{BN}$, (C) USB and (D) locally magnified $\text{SiO}_2@\text{BN}$. EDS elemental analysis of (E) h-BN, (F) $\text{SiO}_2@\text{BN}$, and (G) USB.

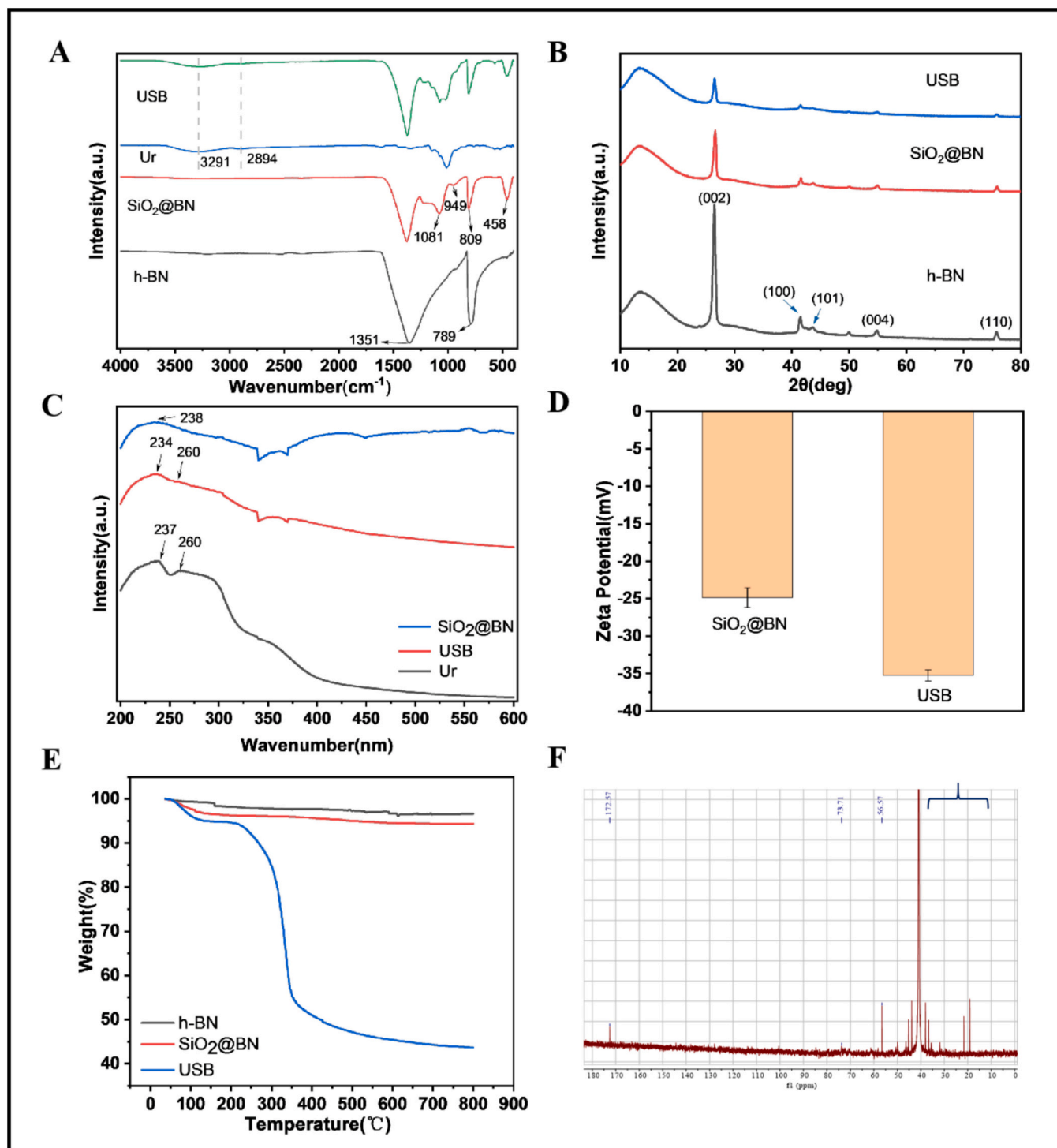


Fig. 3. (A) FTIR spectra of h-BN, SiO₂@BN, Ur, and USB fillers; (B) XRD patterns of h-BN, SiO₂@BN, and USB fillers; (C) UV-vis spectra of Ur, SiO₂@BN, and USB fillers; (D) The Zeta potential of SiO₂@BN and USB fillers. (E) TG curves of h-BN, SiO₂@BN, and USB; (F) Liquid-state ¹³C NMR spectrum of USB.

and 809 cm⁻¹ correspond to the stretching vibration of silanol (Si-OH) and the asymmetric stretching vibration of Si-O-Si bonds, confirming the successful coating of silica onto the BN surface [12]. Compared to SiO₂@BN, the USB composite exhibits new characteristic absorption peaks at 3291 cm⁻¹ and 2894 cm⁻¹, ascribed to vibrations of -CH=CH- and C-H bonds in the alkyl side chains of urushiol. Additionally, characteristic vibrational peaks of the aromatic ring in Ur are visible in the comparative regions marked by gray shading [29,32]. These FTIR results demonstrate that a silica layer was successfully coated onto the h-

BN surface via the sol-gel method, followed by organic modification with Ur through free-radical polymerization.

As shown in Fig. 3B, the XRD patterns of all samples exhibit distinct diffraction peaks corresponding to the (002), (100), (101), (102), (004), and (110) crystal planes, indicating that the hexagonal crystal structure of h-BN was well preserved in the USB composite after multiple processing steps. However, compared to pristine BN, the diffraction peak intensity at the (002) plane progressively decreased in SiO₂@BN and further in the USB composite. This attenuation is attributed to successful

modification with silica, followed by adsorption of Ur onto the BN surface via π - π interactions, hydrogen bonding, and/or coordination effects [29].

To investigate the interaction between $\text{SiO}_2\text{@BN}$ and urushiol(Ur), UV-Vis spectroscopy was conducted. As shown in Fig. 3C, Ur exhibits characteristic absorption peaks at 237 and 260 nm, which are attributed to the π - π^* transitions of the benzene ring and the absorption of conjugated double bonds in the side chain, respectively. The USB composite displays similar absorption features at 234 and 260 nm, suggesting that the structure of Ur remains largely unchanged after composite formation. Notably, the absorption peak corresponding to the π - π^* transition of the benzene ring in the USB composite is blue-shifted to 234 nm, indicating interactions such as coordination, hydrogen bonding, and π - π stacking between $\text{SiO}_2\text{@BN}$ and Ur [33].

The zeta potential was measured to assess the surface charge properties of the particles, which is presented in Fig. 3D. $\text{SiO}_2\text{@BN}$ exhibited a zeta potential of -24.86 ± 1.32 mV. After modification with negatively charged Ur, the zeta potential of the USB composite reached -35.24 ± 0.77 mV. This change suggests an increased density of negative surface charges, thereby improving colloidal stability via enhanced electrostatic repulsion.

Thermogravimetric analysis (TGA) was employed to investigate the thermal stability and composition of the materials (Fig. 3E). The USB

composite exhibited a sharp mass loss of 56.30 % at 800 °C, primarily occurring between 200 and 300 °C due to the thermal decomposition of the surface-immobilized Ur. In contrast, hexagonal boron nitride (h-BN) showed a minimal mass loss of 3.37 %, attributed to the evaporation of adsorbed water. The $\text{SiO}_2\text{@BN}$ intermediate displayed a mass loss of approximately 5.62 %, resulting from the decomposition of surface silanol groups. The substantially greater mass loss of USB, compared to that of $\text{SiO}_2\text{@BN}$, confirms the successful adsorption of Ur onto the composite surface.

The chemical structure was further analyzed using ^{13}C NMR spectroscopy (Fig. 3F). The signal at 172.57 ppm is assigned to the carbonyl carbon ($\text{C}=\text{O}$) of the ester group in MPS. The peak at 73.71 ppm is attributed to the $\text{C}-\text{O}$ carbon, while the carbon adjacent to the $\text{C}=\text{O}$ group appears at 56.57 ppm. Additionally, multiple signals in the range of 40–10 ppm are ascribed to methyl and methylene carbon atoms from both MPS and Ur molecules [21]. These results confirm the successful coating of urushiol onto the $\text{SiO}_2\text{@BN}$ surface, indicating successful preparation of the USB.

2.2. Cross-sectional morphology and dispersion analysis of pristine BN, USB, and their corresponding composite coatings

The dispersion stability of pristine h-BN and the USB composite was

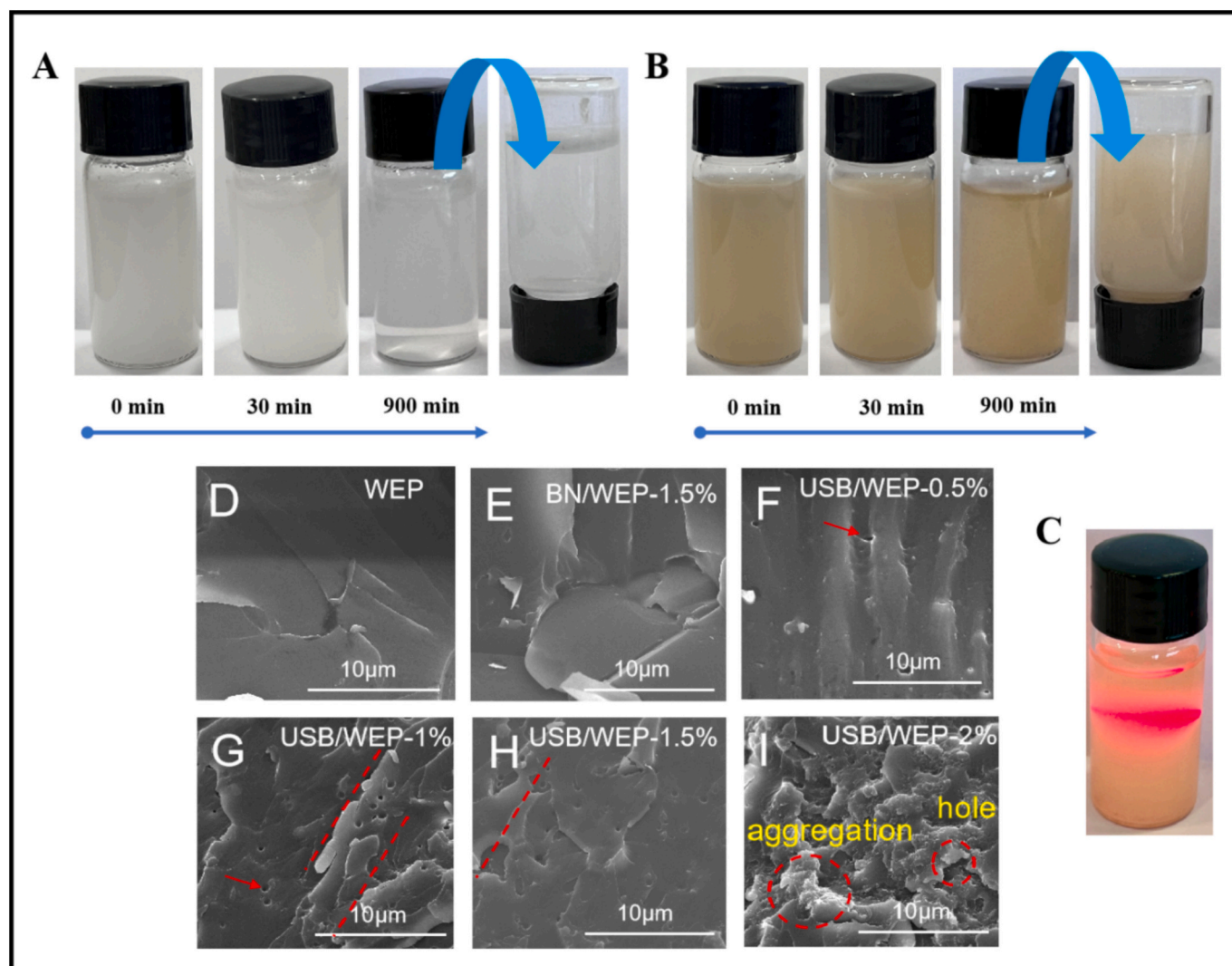


Fig. 4. (A) Optical photographs of dispersibility tests of BN; (B) Optical photographs of dispersibility tests of USB powders; (C) Tyndall Effect Image of Dispersed USB Powder; (D–I) FESEM cross-section photograph of composite coating of WEP, BN/WEP-1.5 %, USB/WEP-0.5 %, USB/WEP-1 %, USB/WEP-1.5 % and USB/WEP-2 %, respectively.

evaluated in propylene glycol monomethyl ether via a long-term settling test. Both h-BN and USB were dispersed at a concentration of approximately 2 mg/mL and left under identical conditions. Their dispersion states were documented at 1 min, 30 min, and 900 min (Fig. 4A, B). After 30 min, significant aggregation was observed at the bottom of the h-BN sample, whereas the USB sample remained homogeneously dispersed. By 900 min, the h-BN dispersion had undergone complete precipitation with a clear supernatant. In contrast, the USB dispersion exhibited only partial sedimentation, highlighting its superior suspension stability. Upon inverting the sample vial, the USB composite could be rapidly redispersed, while the h-BN sample largely remained suspended near the liquid surface or resisted redispersion. This indicates that modification with Ur and SiO₂ significantly enhanced the dispersibility of h-BN in solvents.

The improvement is attributed to the unique hybrid nano-architecture of USB. The exfoliated h-BN possesses nanoscale thickness. An amorphous silica (SiO₂) layer several nanometers thick was precisely constructed on its surface via a sol-gel process. The outermost layer consists of urushiol, which forms a polymeric grafting layer through covalent binding between its catechol groups and surface silanol groups (Si-OH) on SiO₂. This hierarchical structure maintains the overall particle size within the sub-micron range-comparable to the wavelength of visible light-thereby enabling efficient light scattering.

Furthermore, the long alkyl chains (C₁₅-C₁₇) of urushiol form a flexible polymeric protective layer on the particle surface. This layer promotes dispersion stability primarily through steric stabilization: as particles approach, the compression of these extended chains reduces entropy and generates a strong osmotic repulsive force. This mechanism effectively overcomes van der Waals attractive forces and prevents particle aggregation. As a result, the material can exist as stable nanoparticles in solvent over extended periods, forming a homogeneous colloidal dispersion system that exhibits a distinct Tyndall effect (Fig. 4C).

Then, the pristine h-BN and USB composite fillers with varying mass fractions were incorporated into WEP. After uniform dispersion, the mixtures were sprayed onto substrates and cured to form composite coatings. The cross-sectional morphologies of the pure WEP coating, BN/WEP-1.5 % composite coating, and USB/WEP composite coating are shown in Fig. 4D-I.

The pure WEP coating exhibited a smooth fracture surface with multiple microcracks, indicating typical brittle fracture behavior (Fig. 4D). This structural feature facilitates crack propagation under mechanical stress. In the WEP composite coating with unmodified h-BN, severe agglomeration of h-BN was observed, resulting in poor dispersion and accelerated microcrack expansion (Fig. 4E). This phenomenon is primarily attributed to the inherent properties of h-BN: its graphite-like layered structure held by van der Waals forces, high chemical inertness, and lack of hydrophilic functional groups (e.g., -OH, -COOH), leading to strong hydrophobicity and poor wettability in aqueous systems [34,35]. Furthermore, significant differences in surface energy and density between BN and water contribute to inferior interfacial compatibility.

In contrast, the fracture surfaces of composite coatings modified with USB fillers appeared significantly rougher (Fig. 4F-I). This can be attributed to the amphiphilic molecular structure of urushiol, which acts as a “molecular bridge” to enhance the compatibility between the filler and the resin matrix. This improvement promotes interfacial adhesion and effectively impedes crack propagation. As the USB content increased, the number of delicate pores in the coating decreased, and a distinct scale-like morphology emerged, indicating strong interfacial interactions between the USB filler and the epoxy matrix [29]. The red dashed lines in Fig. 4G and H highlight the multi-layered physical barrier structure formed by the layered filler within the coating, which can effectively obstruct the penetration of corrosive agents toward the metal substrate in anti-corrosion applications. When the USB content reached 1.5 wt%, the interface between the filler and the resin became blurred, with the fewest observable pores, demonstrating optimal interfacial

compatibility. However, excessive USB content (e.g., beyond 1.5 wt%) led to filler agglomeration and the formation of larger voids (Fig. 4I), while insufficient content failed to establish an effective “labyrinth” physical barrier pathway, thus compromising the barrier performance of the coating.

2.3. The mechanical properties of the composite coatings

The choice, proportion, and effective dispersion of fillers in the resin substantially affect the mechanical properties of the composite coatings.

As observed in Table 1, the composite coatings incorporated with the USB demonstrate superior mechanical properties compared to that containing conventional h-BN filler at the same doping level. In addition, the mechanical properties of the composite coatings exhibit a distinct trend as the USB content increases. Specifically, both hardness and adhesion demonstrate a monotonic improvement, which is primarily attributed to the uniform dispersion of the filler within the polymer matrix and strong interfacial interactions—such as hydrogen bonding and van der Waals forces—between the filler and the organic resin. These interactions effectively restrict the mobility of polymer molecular chains, thereby enhancing compressive strength and rigidity. Notably, flexibility follows a non-monotonic trend: it decreases initially before increasing with higher filler loading. This behavior is ascribed to the role of the Ur modification layer, which integrates chemically into the epoxy resin's cross-linked network rather than acting as an inert barrier. This integration strengthens the interface between the inorganic filler and the organic matrix. Meanwhile, the long alkyl chains in Ur form a “flexible bridge” between the rigid inorganic phase and the rigid epoxy network, effectively relieving stress concentration and improving toughness. However, flexibility decreases at both extremely low (0.5 wt %) and high (2 wt%) filler contents. Insufficient filler content fails to form a continuous reinforcing network, whereas excessive filler content leads to agglomeration and defects (e.g., pores), thereby degrading the overall performance. Additionally, silanol groups (Si-OH) on the SiO₂ surface form hydrogen bonds with the cured epoxy resin, synergistically enhancing interfacial adhesion and further restricting polymer chain mobility—ultimately contributing to improved hardness and adhesion properties [36–39].

To summarize, the incorporation of the USB filler significantly enhances interfacial bonding between the epoxy matrix and the filler, resulting in composite coatings with superior comprehensive mechanical properties and durability. Based on the balanced optimization of multiple performance indicators, the USB/WEP-1.5 % coating was identified as the optimal system, exhibiting the best overall mechanical performance. Although evaluation of tensile properties via stress-strain curves could provide further insights, the suite of coating-specific mechanical tests presented here—hardness, flexibility, adhesion, and impact resistance—is considered more directly relevant for assessing performance in the primary application as protective coatings.

Table 1
The mechanical properties of the composite coating with different filler content.

	WEP	BN/ WEP- 1.5 %	USB/ WEP- 0.5 %	USB/ WEP-1 %	USB/ WEP- 1.5 %	USB/ WEP-2 %
Hardness	HB	HB	HB	H	H	H
Flexibility (mm)	1	1.5	1	0.5	0.5	1
Impact resistance (kg.cm)	50	50	50	50	50	50
Adhesion (MPa)	2.21	1.84	2.33	2.42	2.49	2.57

2.4. The surface properties of the coating

The incorporation of USB fillers markedly influences the surface characteristics of the composite coatings. As illustrated in Fig. 5, the coatings exhibit enhanced hydrophobicity, evidenced by a significant increase in the water contact angle from 98° to 111° with rising USB filler content. Correspondingly, the surface free energy of the coating—determined using diiodomethane probe measurements and summarized in Table 2—shows a pronounced decrease as the USB content increases. This improvement can be attributed to two main factors: first, the hydrophobic alkyl chains (C15–C17) of urushiol grafted onto the boron nitride surface contribute to intrinsic water repellency; second, the uniform dispersion of USB fillers within the coating matrix creates nanoscale mastoid-like microstructures, imparting a quasi-lotus effect. As a result, both the contact angle and the hydrophobicity increase, while the surface tension decreases progressively with higher filler loading.

2.5. The thermal conductivity of the composite coating

The present study focuses on achieving effective doping and dispersion of composite fillers within the resin matrix to enhance the thermal conductivity of the coating. Investigating the regularity of thermal conductivity changes in the coating under these modifications provides essential data for evaluating the effectiveness of the filler integration strategy.

As presented in Fig. 6, the significant enhancement in the through-thickness thermal conductivity of the USB-filled composite coatings is primarily attributed to the incorporation of hexagonal boron nitride (h-BN), which exhibits intrinsic high thermal conductivity. Specifically, Fig. 6A presents measurements performed on coatings with different USB filler loadings to quantify this enhancement. Quantitative analysis of these measurements revealed a substantial increase in thermal conductivity as the USB content increased. For instance, the USB/WEP-1.5 % coating exhibited a thermal conductivity of $0.4712 \text{ W/(m}\cdot\text{K)}$, representing an 86 % enhancement compared to the pure WEP coating ($0.2529 \text{ W/(m}\cdot\text{K)}$).

This improvement can be ascribed to two main factors: the uniform dispersion of the USB filler within the epoxy matrix and the inherent high thermal conductivity of the BN nanosheets [40]. The homogeneous distribution of USB particles facilitates the formation of continuous and efficient heat-transfer pathways, while the BN components serve as primary channels for phonon transport. Supplementary infrared thermography analysis provided further evidence (Fig. 6B), demonstrating a

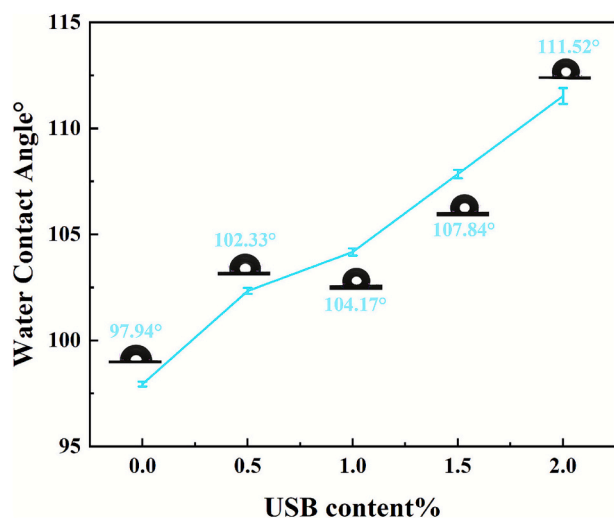


Fig. 5. Variation trend of surface contact angle with different component ratio in the composite coatings with different USB filler content.

Table 2

The surface tension properties of the composite coatings with different filler content.

Sample	Dispersive component (γ_s^d)	Polar component (γ_s^p)	Surface free energy (γ_s)
WEP	35.28mN/m	0.26mN/m	35.54mN/m
USB/WEP-0.5 %	32.11mN/m	0.10 mN/m	32.21 mN/m
USB/WEP-1 %	29.72 mN/m	0.09 mN/m	29.79mN/m
USB/WEP-1.5 %	27.25 mN/m	0.04 mN/m	27.29 mN/m
USB/WEP-2 %	24.80 mN/m	0.01 mN/m	24.81 mN/m

clear positive correlation between USB content and the rate of surface temperature increase. After 30 s of thermal exposure, the surface temperature of the pure WEP coating reached 70.0°C , whereas coatings containing 0.5 wt%, 1 wt%, 1.5 wt%, and 2.0 wt% USB filler attained temperatures of 82.2°C , 87.1°C , 91.6°C , and 95.8°C , respectively. The nearly linear relationship between filler loading and temperature rise underscores the role of BN in establishing an effective thermal conduction network within the composite, thereby markedly improving the overall thermal management performance of the epoxy resin [15,41,42].

2.6. The corrosion resistance of the composite coating

To investigate the corrosion inhibition mechanism of USB-modified fillers on Q235 steel substrates, two types of dispersions were prepared: a pristine boron nitride (h-BN) dispersion and a USB composite filler dispersion [43]. Both were uniformly dispersed in deionized water with a solid content of 100 mg/L, and 3.5 wt% sodium chloride was added to simulate a corrosive medium. After immersing Q235 steel electrodes in each solution for 24 h, corrosion behavior was systematically evaluated using potentiodynamic polarization curves. Fig. 7A shows potentiodynamic polarization curves of Q235 steel in different systems after immersion.

As exemplified by data in Table S1, results reveal that compared to blank and pristine BN groups, samples with USB filler exhibited significantly lower I_{corr} and corrosion rate (C.R.), decreasing from $1.6388 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$ to $8.3824 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$ and $2.6855 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$, respectively, demonstrating adequate corrosion protection provided by USB filler. The corrosion protection mechanism primarily arises from synergistic effects of two aspects: (1) BN nanosheets form a dense physical barrier film on the metal surface, effectively delaying penetration of corrosive species and providing barrier protection. Furthermore, unlike conductive graphene, BN is an insulator, avoiding the formation of galvanic corrosion cells with the metal substrate and reducing the risk of electrochemical corrosion. (2) Catechol groups in urushiol chelate iron ions produced during corrosion, forming a passive film-like protective layer at the metal interface, further retarding corrosion. This demonstrates that USB filler significantly enhances corrosion protection performance for Q235 steel through dual mechanisms of physical shielding and metal ion chelation.

Fig. 7B compares the Tafel polarization curves of the pristine WEP coating and composite coatings incorporated with different loadings of USB fillers after immersion in a 3.5 wt% NaCl solution. The changes in the slopes of the anodic and cathodic branches indicate that the introduction of USB fillers significantly alters the corrosion inhibition mechanism of the coatings. According to the attached table (Table S2 Supporting Information), when the USB filler content is 1.5 wt% (USB/WEP-1.5 %), the corrosion current density (i_{corr}) reaches a minimum value of $8.398 \times 10^{-8} \text{ A/cm}^2$, nearly two orders of magnitude lower than that of the pure WEP coating ($3.256 \times 10^{-6} \text{ A/cm}^2$), indicating a significant improvement in anti-corrosion performance. Further analysis

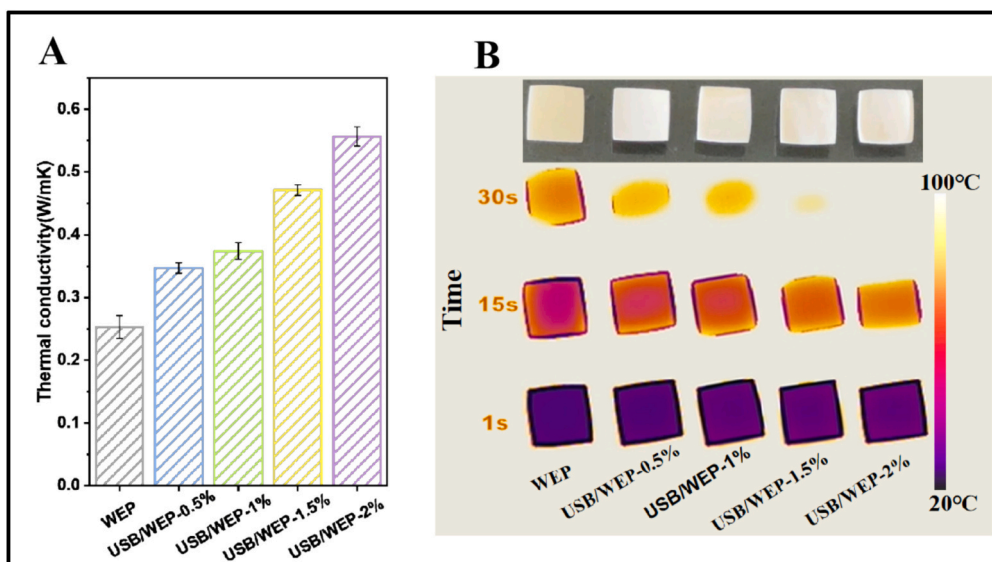


Fig. 6. (A) Thermal conductivity of the different USB filler content; (B) Infrared thermographic images of the composite coatings (the digital photographs of the corresponding samples are shown in the top insets).

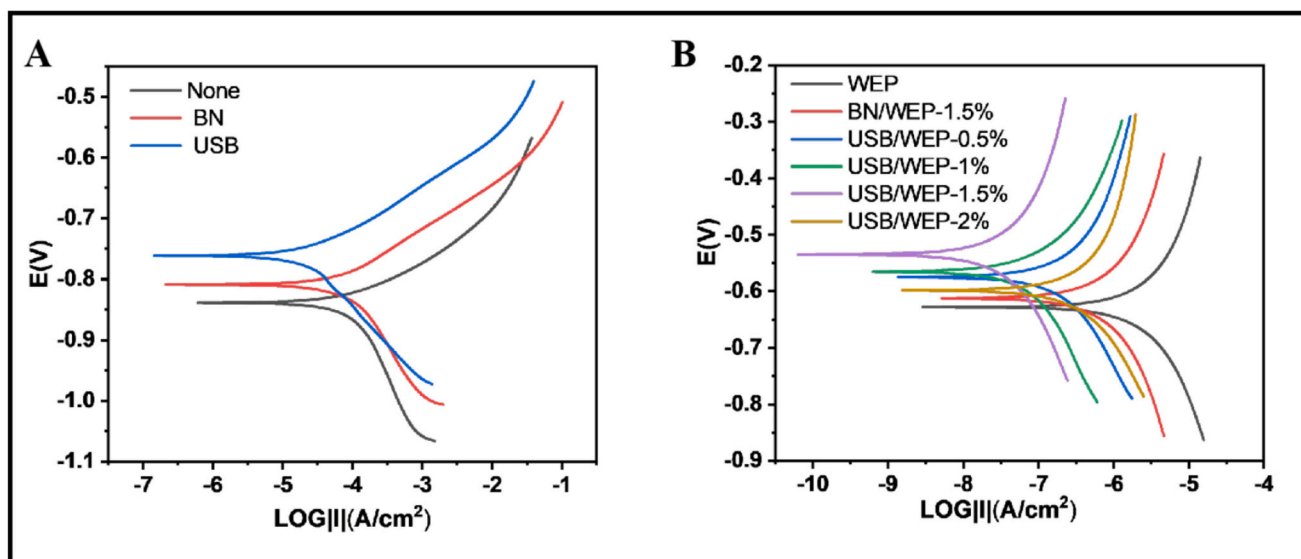


Fig. 7. (A) Polarization curve of Q235 steel plate immersed in 3.5 wt% NaCl aqueous solution without and with BN and USB for 24 h; (B) Comparison of polarization curves of WEP, BN/WEP-1.5 %, USB/WEP-0.5 %, USB/WEP-1 %, USB/WEP-1.5 % and USB/WEP-2 % coatings after immersion in 3.5 wt% (wt%) sodium chloride (NaCl) aqueous solution for 270 h.

of the Tafel slopes reveals that all composite coatings exhibit higher cathodic Tafel slopes (β_c) compared to the pure WEP coating ($\beta_c \approx 86.4$ mV/dec). Among them, the β_c value of the USB/WEP-1.5 % coating increases to 303.9 mV/dec, suggesting a substantially enhanced activation energy barrier for the cathodic oxygen reduction reaction (ORR). This improvement is mainly attributed to two factors: (1) Physical barrier effect: The two-dimensional silica-coated BN nanosheets effectively extend the diffusion path of corrosive agents such as O_2 and Cl^- , creating a “labyrinth effect”; (2) Chemical oxygen scavenging: The active phenolic hydroxyl groups in urushiol molecules effectively remove dissolved oxygen, reducing the oxygen concentration at the metal/coating interface [24]. Simultaneously, the anodic Tafel slope (β_a) of this coating increases from 174.7 mV/dec for the pure WEP to 533.9 mV/dec, indicating significant suppression of the anodic metal dissolution reaction. This enhancement can be attributed to: (1) The chelation of urushiol with dissolved Fe^{2+} to form insoluble complexes, promoting the

formation of a passivation layer that blocks anodic active sites; (2) The migration of USB fillers within the coating seals micro-pores and defects, enhancing the coating’s denseness and preventing electrolyte penetration [26]. At the optimal loading of 1.5 wt%, the β_c/β_a ratio is approximately 0.57, indicating that the corrosion process is dominated by a mixed control mechanism with more significant anodic suppression. In addition, the corrosion potential (E_{corr}) shifts positively from -0.641 V for the pure WEP to -0.546 V, further demonstrating that the USB filler improves the thermodynamic stability of the coating system. However, when the USB content increases to 2.0 wt%, the corrosion current density (i_{corr}) rises to 8.742×10^{-7} A/ cm^2 , while β_c and β_a decrease to 158.5 mV/dec and 205.8 mV/dec, respectively. The main reasons for this performance degradation include: (1) Agglomeration of fillers at high concentrations, leading to coating defects and accelerated infiltration of corrosive media; (2) Reduced dispersion stability of USB in the epoxy resin, compromising the coating’s integrity and accelerating

both anodic and cathodic reactions at the interface.

So an appropriate amount of USB filler significantly enhances the anti-corrosion performance of the waterborne epoxy coating through a synergistic effect of physical barrier and electrochemical inhibition, whereas excessive filler content deteriorates protective performance due to compromised coating structural integrity.

Electrochemical impedance spectroscopy (EIS), a non-destructive and highly sensitive analytical technique, was employed to evaluate the dynamic protective behavior of organic coating/metal systems during long-term exposure to corrosive medium, owing to its capability to effectively quantify barrier properties, defect evolution, and interfacial electrochemical reactions. Corrosion resistance of USB-modified filler-reinforced WEP-based composite coatings after 270 h immersion in 3.5 wt% NaCl solution was systematically investigated using pure WEP and unmodified BN/WEP-1.5 % coatings as references with particular emphasis on USB/WEP-1.5 % and USB/WEP-2.0 % systems. Results confirm that excellent protective performance can be achieved through optimized filler modification and dispersion and reveal underlying mechanisms across multiple scales.

The Nyquist plots (Fig. 8A1-F1) clearly reveal differences in the electrochemical behavior of various coating systems: Both pure WEP coatings and BN/WEP-1.5 % coatings exhibited a diffusion tail with a 45° slope during the initial 24 h of immersion, indicating rapid electrolyte penetration and subsequent corrosion initiation at the substrate interface [44,45]. In contrast, the USB/WEP-1.5 % coating maintained nearly ideal capacitive arcs throughout the 270-h test period, demonstrating excellent dielectric properties and structural integrity. This performance enhancement is primarily attributed to the highly dispersed modified h-BN nanosheets, which form a labyrinth-like barrier structure that significantly prolongs the diffusion path of corrosive agents. Analysis based on the Warburg coefficient showed that 3–4 orders of magnitude reduced the diffusion coefficient of the USB/WEP-1.5 % coating compared to pure WEP coatings. The USB/WEP-2.0 % system exhibited transitional behavior after 96 h of immersion; its capacitive arcs became distinctly distorted, with emerging diffusion characteristics, suggesting that agglomeration of USB fillers caused stress concentration and microcrack formation, providing rapid pathways for electrolyte infiltration.

Bode magnitude plots (Fig. 8A2-F2) further provided quantitative evidence of impedance performance. After being immersed for 270 h, low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) showed USB/WEP-1.5 % retained value of $2.33 \times 10^{10} \Omega\cdot\text{cm}^2$, approximately four orders of magnitude higher than pure WEP ($7.89 \times 10^5 \Omega\cdot\text{cm}^2$) and BN/WEP-1.5 % ($6.64 \times 10^6 \Omega\cdot\text{cm}^2$), indicating nearly complete suppression of Faradaic reactions at the interface. In comparison, the impedance of USB/WEP-2.0 % decreased to $1.07 \times 10^7 \Omega\cdot\text{cm}^2$, implying excessive filler content induced galvanic effects, accelerating interfacial corrosion [46].

Phase angle spectra (Fig. 8A3-F3) offered critical insights into interfacial status within the mid-frequency range (1–100 Hz). USB/WEP-1.5 % coating maintained a broad plateau around -80 to -85 throughout immersion, indicating nearly ideal capacitive behavior with minimal dielectric relaxation. Constant phase element exponent ($n > 0.98$) further confirmed high coating homogeneity. In contrast, pure WEP and BN/WEP-1.5 % coatings showed noticeably narrowed phase peaks shifting toward higher frequencies, reflecting ongoing hydration and performance degradation. USB/WEP-2.0 % system exhibited second time constant after 96 h, signifying initiation of interfacial corrosion reactions where local acidification and concentration polarization intensified metal dissolution.

Further analysis via equivalent circuit fitting (Fig. 9A-D and Table S3) revealed that after 270 h immersion, the coating resistance (R_c) of USB/WEP-1.5 % was $2.74 \times 10^9 \Omega\cdot\text{cm}^2$, significantly higher than pure WEP ($7.6 \times 10^4 \Omega\cdot\text{cm}^2$) and BN/WEP-1.5 % ($2.62 \times 10^6 \Omega\cdot\text{cm}^2$). Its charge transfer resistance (R_{ct}) reached $2.10 \times 10^{10} \Omega\cdot\text{cm}^2$, exceeding reference groups by 4–5 orders of magnitude, demonstrating both

superior physical barrier properties and interfacial chemical passivation capability. R_c and R_{ct} values of USB/WEP-2.0 % were $1.21 \times 10^6 \Omega\cdot\text{cm}^2$ and $4.57 \times 10^7 \Omega\cdot\text{cm}^2$, respectively, indicating noticeably anticorrosion performance.

To elucidate the physical significance of the equivalent circuit elements and the coating degradation mechanism, a detailed interpretation of the models (Fig. 9A, B) is provided herein. The selection of equivalent circuits was based on the distinct electrochemical responses observed during immersion. The simple R(QR) circuit (Fig. 9A) was employed for coatings exhibiting a single time constant throughout the immersion period (e.g., USB/WEP-1.5 %), which signifies an intact barrier with negligible electrolyte penetration to the metal substrate. For coatings developing a second time constant (e.g., pure WEP and BN/WEP-1.5 % after 24 h), the R(QR(QR)) model (Fig. 9B) was applied. In this model: R_s represents the solution resistance; the parallel combination of the coating constant phase element (Q_c) and the coating resistance (R_c) characterizes the protective polymer layer. The use of Q_c , instead of an ideal capacitor, accounts for the frequency dispersion arising from surface heterogeneity, porosity, and thickness variation within the coating. R_c quantifies the resistance against electrolyte penetration through coating defects, serving as a critical indicator of barrier integrity. The second time constant, composed of the double-layer constant phase element (Q_{dl}) and the charge transfer resistance (R_{ct}), describes the electrochemical corrosion process at the metal/coating interface. Q_{dl} represents the capacitance of the electrical double layer formed at the metal surface where electrolyte has permeated, while R_{ct} quantifies the resistance to faradaic reactions, including anodic metal dissolution and cathodic oxygen reduction. A high R_{ct} value indicates effective suppression of corrosion reactions at the interface. In certain cases (e.g., pure WEP at early stages), a Warburg diffusion element (Z_w) was incorporated to model the diffusion-controlled transport of corrosive species such as O_2 and Cl^- .

The temporal evolution of EIS parameters (Table S3) delineates three distinct stages of coating degradation in 3.5 wt% NaCl solution over 270 h:

2.6.1. Initial barrier stage (0–12h)

All coatings exhibited high R_c and R_{ct} values with a single, high-frequency time constant in the phase angle plots (Fig. 7A3-F3), indicating effective physical barrier properties that impeded electrolyte ingress.

2.6.2. Electrolyte uptake and interface corrosion initiation stage (24–96 h)

For less protective coatings (e.g., pure WEP, BN/WEP-1.5 %), R_c decreased markedly while Q_c increased due to water uptake (dielectric constant of $H_2O \approx 80$) displacing air ($\epsilon \approx 1$) within the coating pores. The emergence of a second time constant (Q_{dl} and R_{ct}) signified that the electrolyte had reached the metal substrate, initiating interfacial corrosion reactions.

2.6.3. Active corrosion and protection failure stage (270 h)

At this terminal stage, the pure WEP coating showed drastically reduced R_c and R_{ct} values ($\sim 10^5 \Omega\cdot\text{cm}^2$), confirming a complete loss of protective function. In contrast, the optimal USB/WEP-1.5 % coating maintained a single time constant and exceptionally high impedance ($R_c > 10^9 \Omega\cdot\text{cm}^2$, $R_{ct} > 10^{10} \Omega\cdot\text{cm}^2$) throughout the immersion period, demonstrating outstanding long-term stability.

Notably, a strong correlation exists between the electrochemical parameters and the coating microstructure. The ultra-high R_c and R_{ct} values of the USB/WEP-1.5 % coating are directly attributed to its uniform, pore-free morphology and the “labyrinth effect” created by the well-dispersed USB fillers, as evidenced in the FESEM cross-section (Fig. 4H).

Capacitance parameter variations also mirrored the durability of the coating: for USB/WEP-1.5 %, the constant phase element parameter (Q_c) remained stable at approximately $2.29 \times 10^{-11} \text{S}\cdot\text{cm}^{-2}$, while its double-

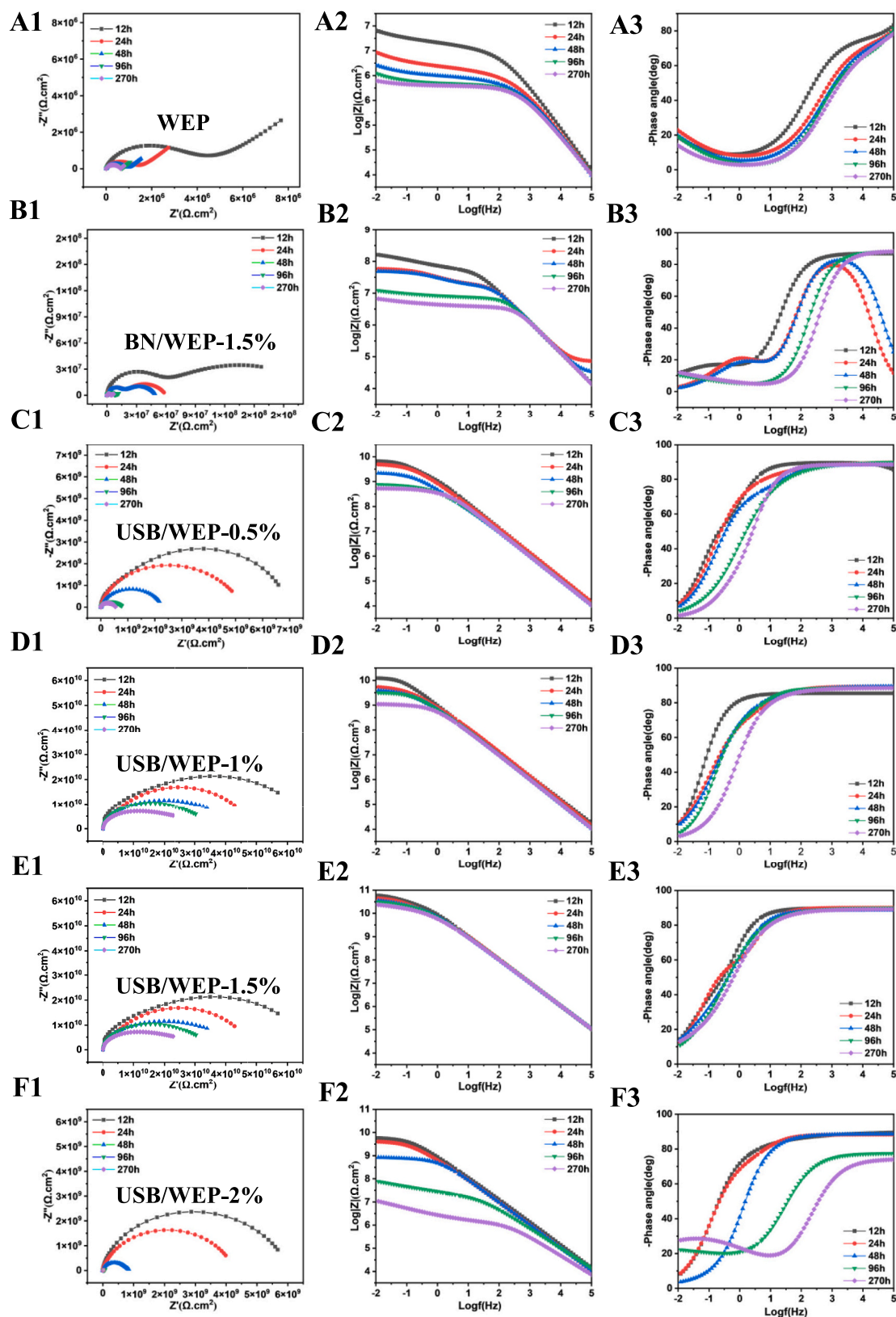


Fig. 8. Evolution of electrochemical impedance behavior for USB/WEP coatings during prolonged corrosion exposure(270 h) (A) WEP coating; (B) BN/WEP-1.5 %; (C) USB/WEP-0.5 %;(D)USB/WEP-1 %;(E) USB/WEP-1.5 %;(F) USB/WEP-2 %; (A1 ~ F1) Nyquist; (A2 ~ F2) Bode magnitude; (A3 ~ F3) phase angle representations.

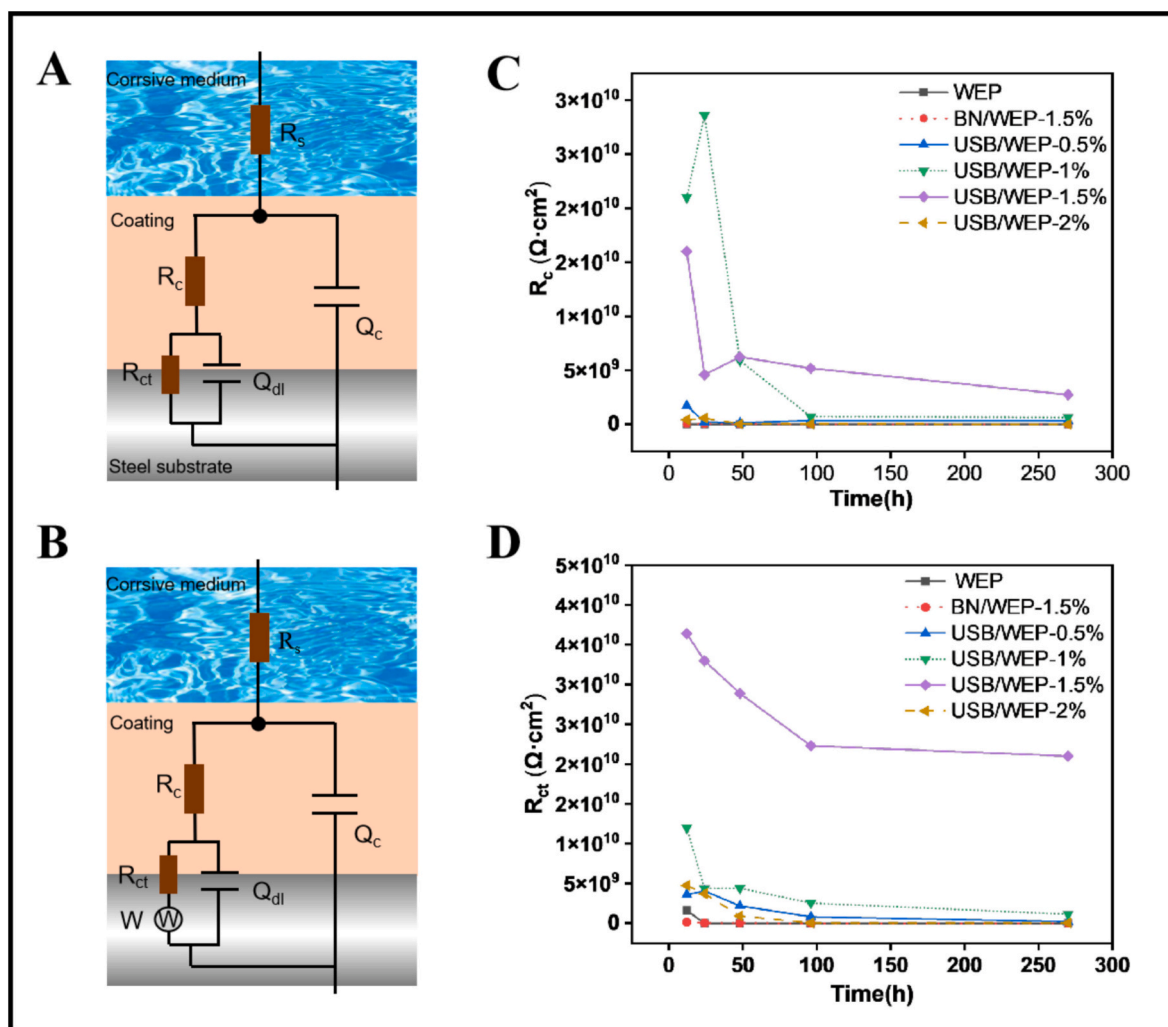


Fig. 9. (A, B) The equivalent circuits used to fit the EIS results of coatings in different stages; (C, D) time-dependent property of R_c (C) and R_{ct} (D) of USB/WEP coatings with different content of USB immersion in 3.5 wt% NaCl solution.

layer capacitance (C_{dl}) stayed below $5 \text{ nF} \cdot \text{cm}^{-2}$ -findings that indicate minimal water absorption and an intact interface. In contrast, the Q_c value of pure WEP increased steadily from $1.07 \times 10^{-9} \text{ S} \cdot \text{cm}^{-2}$ to $2.64 \times 10^{-9} \text{ S} \cdot \text{cm}^{-2}$, a trend that points to progressive plasticization and hydration.

Exceptional performance of USB/WEP-1.5 % originates from multi-scale synergistic mechanisms. At the nanoscale, exfoliated h-BN forms a highly tortuous network, extending the diffusion path by 10–100 times compared to unfilled coatings. At the interface, urushiol modification not only improves dispersion and adhesion of h-BN but also effectively blocks hydrated chloride ions (diameter $\approx 0.66 \text{ nm}$) through the molecular sieving effect. At the molecular level, catechol groups in urushiol effectively chelate metal ions via coordination with $\text{Fe}^{2+}/\text{Fe}^{3+}$, suppressing cathodic reactions. Their antioxidant activity modulates local pH, and under an electric field, they self-assemble into a dense organic layer at defects, increasing the electron transfer energy barrier. Tafel-like behavior observed in the low-frequency region further suggests the possible formation of a semiconducting urushiol-iron composite film, altering the interfacial electronic structure.

In conclusion, this electrochemical analysis demonstrates that the USB/WEP-1.5 % coating, with optimized filler content and dispersion, constructs a multifunctional barrier system that outperforms conventional coatings by several orders of magnitude. This study provides key design principles for next-generation anti-corrosion coatings: balancing filler content to avoid percolation while maximizing tortuosity;

employing multifunctional modifiers combining dispersion stability and passivation potential; constructing hierarchical structures operating synergistically across multiple scales.

2.7. Anticorrosion mechanism of the USB/WEP coating

To investigate changes in elemental composition and chemical states of USB-modified coating during corrosion and reveal the protection mechanism, XPS analysis was conducted on the exposed substrate surface at scribed areas of WEP coating and USB/WEP-1.5 % composite coating after 40 days of immersion in a 3.5 wt% NaCl solution.

As shown in Fig. 10A, O 1s spectra of both coatings exhibit distinct characteristic peaks. In WEP coating, the central peak at 531.5 eV is attributed to common C=O and C—O functional groups in polymers. In USB/WEP-1.5 %, In contrast, the O 1s spectrum of the USB/WEP-1.5 % coating shows a significant negative shift of approximately 0.7 eV to a lower binding energy of 530.8 eV. This shift indicates an increase in electron density around the oxygen atoms, providing direct spectroscopic evidence for coordination bonding between oxygen-containing functional groups (e.g., catechol in urushiol) and metal ions (e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$), thereby strongly supporting the chelation effect at the interface. Fig. 10B compares the iron chemical states in scribed areas, quantitatively confirming urushiol's reducing capability. Peak deconvolution revealed a dramatic increase in Fe^{2+} proportion from 22.2 % (pure WEP) to 58.8 % (USB/WEP-1.5 %), while Fe^{3+} decreased from

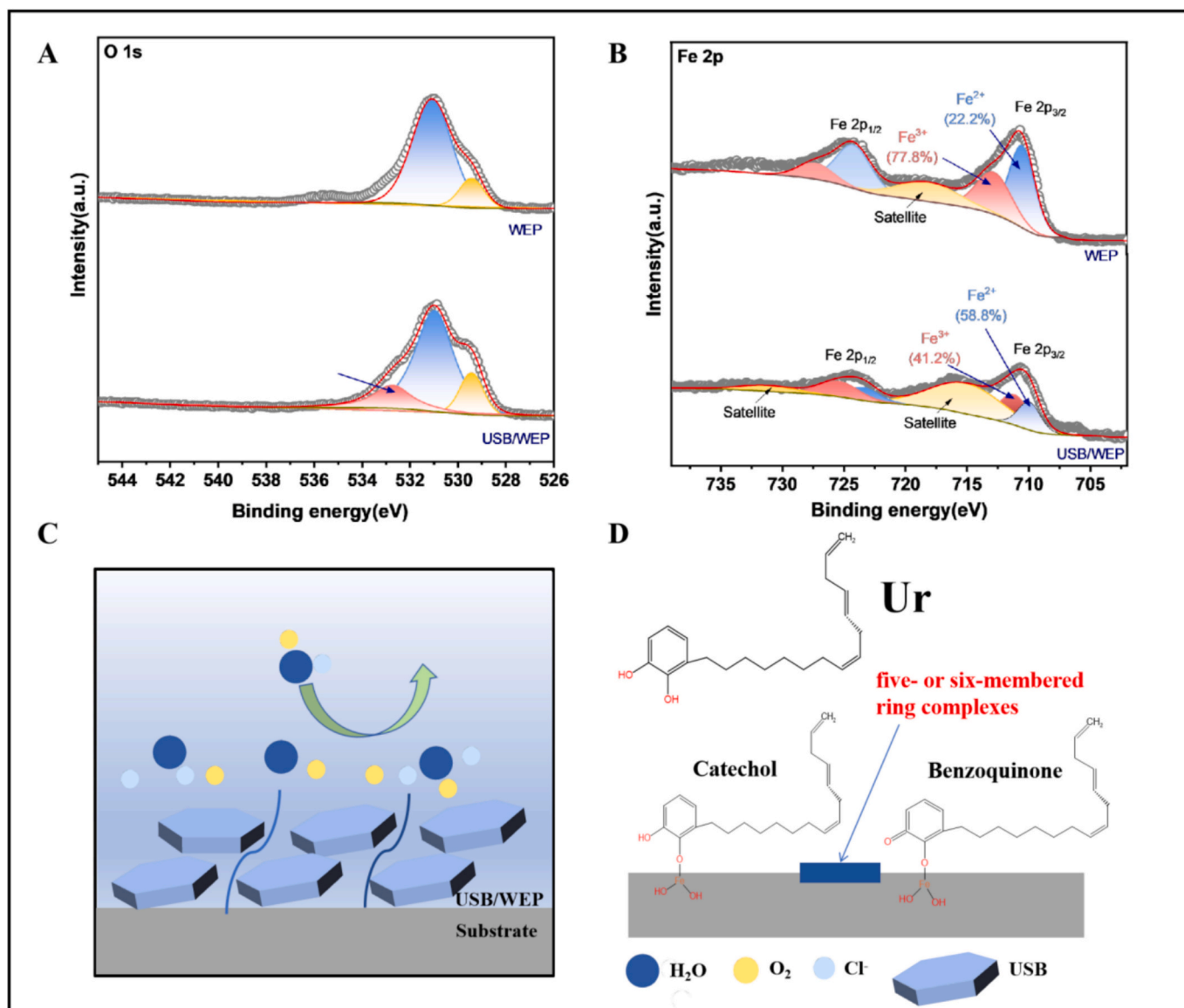
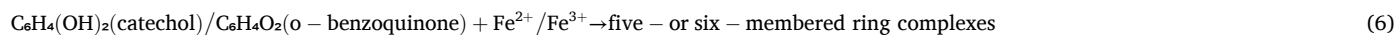
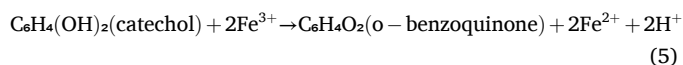
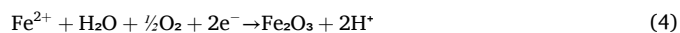


Fig. 10. XPS (A) O 1s and (B) Fe 2p fine spectra of the exposed region of the scratched WEP and USB/WEP composite coatings after 7 days of immersion in 3.5 % NaCl aqueous solution. The anticorrosion mechanism of the USB/WEP coating. (C) Schematic diagram. (D) Molecular structural formula.

77.8 % to 41.2 %. This significant Fe³⁺-to-Fe²⁺ conversion demonstrates urushiol's effective reduction behavior. Moreover, the narrowed Fe 2p_{3/2} peak (reduced FWHM) in USB/WEP-1.5 % indicates a more uniform iron chemical environment, consistent with the formation of well-defined five- or six-membered chelate complexes with urushiol, rather than mixed oxides/hydroxides. These XPS results provide direct evi-



dence that USB filler functions through combined reduction and chelation mechanisms can be summarized as follows [47–49]:



USB/WEP coating exhibits excellent corrosion protection performance originating from the synergistic effect of two mechanisms (Fig. 10C-D): (1) Physical Barrier Effect: Urushiol-modified BN nano-sheets are uniformly dispersed within the coating, forming a labyrinth-like physical barrier significantly prolonging the diffusion path of water, oxygen, and corrosive ions. Consistent with significantly

increased impedance values in electrochemical impedance spectra. (2) Chemical Passivation and Interfacial Chelation: When Q235 steel substrate undergoes corrosion, urushiol component implements a multi-inhibition mechanism through chelation and reduction reactions at the corrosion interface: (i) Reduces highly reactive Fe^{3+} ions in solution and chelates them into stable Fe^{2+} complexes, blocking the corrosion chain reaction. (ii) Forms dense $\text{Fe}^{2+}/\text{Fe}^{3+}$ -organic chelation layer (existing as stable five- or six-membered ring complexes) at active metal sites. This layer effectively covers anodic reaction sites, inhibits metal dissolution, and constitutes a robust physico-chemical composite barrier preventing further penetration of corrosive media.

2.8. Comprehensive comparison of thermally conductive and anticorrosion performance

To identify the optimal coating combining high thermal conductivity (TC) and superior anti-corrosion performance, a systematic comparison was conducted. As shown in Table S4, the USB/WEP-1.5 % coating achieves a thermal conductivity of 0.4712 W/(m·K). This value exceeds that of the M – BNNSs/EP system (0.45 W/(m·K)), confirming the effectiveness of the urushiol-based hybrid filler in constructing efficient heat transfer pathways. More notably, the USB/WEP-1.5 % coating demonstrates exceptional corrosion resistance. After 270 h of immersion, its low-frequency impedance modulus reaches $2.33 \times 10^{10} \Omega\text{-cm}^2$. In contrast, the reported M – BNNSs/EP coating only achieves approximately $10^4 \Omega\text{-cm}^2$ after a shorter immersion period (120h). This represents an improvement of several orders of magnitude, highlighting the significantly enhanced long-term barrier properties provided by the USB filler through synergistic physical barrier and chemical passivation mechanisms.

3. Conclusion

This study successfully developed a novel urushiol-modified silica-coated boron nitride hybrid filler (USB) and incorporated it into a waterborne epoxy (WEP) coating to achieve synergistic enhancement in thermal conductivity and corrosion resistance. The USB filler was fabricated through a multi-step process involving SiO_2 coating via sol-gel and subsequent functionalization with urushiol, which significantly improved its dispersion stability and interfacial compatibility within the polymer matrix. The USB filler was first systematically characterized using techniques such as Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Subsequently, the USB filler was added to the waterborne epoxy resin matrix to prepare the composite coating. When the USB content was 1.5 wt% (denoted as the USB/WEP-1.5 % coating), the comprehensive performance of the composite coating reached its optimum: hardness increased from grade HB to grade H, flexibility improved from 1 mm to 0.5 mm, and thermal conductivity rose from 0.2529 W/(m·K) to 0.4712 W/(m·K), representing an increase of approximately 86 %. Combined with the systematic characterization of the filler, the performance enhancement is primarily attributed to the synergistic effect between the hydrophilic catechol groups and the hydrophobic long alkyl chains in urushiol, as well as multiple interactions such as π - π stacking, hydrogen bonding, and coordination with SiO_2 @BN.

After immersing the coating in a 3.5 wt% NaCl solution for 270 h, its low-frequency impedance modulus reached $10^{10} \Omega\text{-cm}^2$, which is five orders of magnitude higher than that of the pure WEP coating. The corrosion current density significantly decreased from $3.256 \times 10^{-6} \text{ A/cm}^2$ to $8.398 \times 10^{-8} \text{ A/cm}^2$, demonstrating excellent anti-corrosion performance. Crucially, XPS analysis provided direct and quantitative evidence for the proposed active protection mechanism. It was confirmed that the USB coating promotes the conversion of corrosive Fe^{3+} to Fe^{2+} , increasing the Fe^{2+} fraction from 22.2 % to 58.8 % at the defect site. Concurrently, the observed negative shift in the O 1s binding energy and the narrowing of the Fe 2p peaks confirmed the formation of

a stable $\text{Fe}^{2+}/\text{Fe}^{3+}$ -organic chelation lay. This chelation layer, existing in the form of five- or six-membered chelates, effectively covers active corrosion sites, forming a dense passivation barrier.

The USB/WEP coating system developed in this study demonstrates excellent thermal conductivity, mechanical properties, and active-passive synergistic anti-corrosion capability. This material exhibits strong applicability under harsh conditions, such as high temperatures, high humidity, and high salt spray, making it particularly suitable for surface protection of key components in desalination equipment. It can significantly enhance the durability and operational efficiency of such equipment. This research presents a novel approach to designing multifunctional integrated coating materials, which holds important value for industrial applications and promotion.

CRediT authorship contribution statement

Wenguang Lu: Writing – original draft, Formal analysis. **Xiaomei Wang:** Investigation, Data curation, Conceptualization. **Jinbiao Wang:** Investigation. **Zihan Lin:** Software. **Ruofei Liu:** Validation. **Lizhuang Chen:** Methodology. **Zhaolei Li:** Validation. **Zhengbai Zhao:** Visualization. **Weili Li:** Writing – review & editing, Supervision.

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.2025.109819>.

Data availability

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

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