

Synergistic construction of a dual physical barrier in waterborne acrylic coatings via NMA/HEA crosslinking and WCR encapsulation for superior corrosion resistance

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ABSTRACT

Metal corrosion leads to substantial economic losses and severe safety risks, rendering the development of eco-friendly and high-efficiency waterborne anticorrosive coatings an urgent research priority. Waterborne acrylic resins, as mainstream environmentally benign binders, were plagued by inherent drawbacks including poor water resistance, insufficient adhesion, and inadequate long-term corrosion protection, which limited their application in harsh service environments. In this study, an innovative modification strategy was proposed to address these deficiencies: N-methylolacrylamide (NMA) and 2-hydroxyethyl acrylate (HEA) were copolymerized to design and synthesize a self-crosslinkable acrylic latex (N-HAR-X), and it acted as vesicle templates to form composites with waterborne chlorinated rubber (WCR) via hydrophobic adsorption, fabricating a series of N-HAR-X/WCR-Y composite coatings. This encapsulation strategy, distinct from the conventional simple blending of latexes, the formation of composite latex particles via an encapsulation approach not only helped to improve the stability of the system but also enabled the formation of composite paint films with a uniform, flat surface and consistent performance. The results indicated that the NMA/HEA crosslinking network formed a dense three-dimensional structure in the coatings, constructing an excellent physical barrier against corrosive media. Meanwhile, the co-blended film formation of WCR not only enhanced the hydrophobicity of the coating matrix, but strong van der Waals forces between chlorine atoms in WCR molecules also optimized the mechanical properties of the coatings, inhibited the penetration of corrosive media, significantly suppressed the interfacial electrochemical corrosion reaction, and simultaneously improved the wet adhesion of the coatings to metal substrates. Systematic performance characterization demonstrated that the composite coating with 1.5 wt% NMA and 15 wt% WCR achieved the optimal comprehensive performance, exhibiting a pencil hardness of 2H (GB/T 6739–2006), and an abrasion mass loss of merely 0.0198 g after 500 cycles under a rubber wheel abradant (JM-V) according to ISO 7784–2:1997, and a low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) remaining above $10^{10} \Omega \cdot \text{cm}^2$ even after 60 days of immersion in a 3.5 wt% NaCl solution. This work establishes a novel theoretical foundation and provides a feasible technical approach for the design and preparation of high-performance, eco-friendly waterborne organic anticorrosive coatings adapted to harsh service conditions.

1. Introduction

Corrosion is a pervasive threat to metallic materials, causing structural damage, shortened service life, safety accidents, economic losses, and resource wastage, making corrosion protection a longstanding core research focus in materials science [1–3]. For long-service metal

structures in harsh environments (e.g., marine, chemical facilities, infrastructure), high-efficiency anticorrosive technologies are indispensable [4]. With heightened environmental awareness and stricter regulations, traditional high-VOC solvent-borne coatings are severely restricted, driving the inevitable trend toward eco-friendly low-/zero-VOC waterborne anticorrosive coatings as a key direction for green

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sustainable development [5,6].

As a mainstream binder for waterborne anticorrosive coatings, waterborne acrylic resins offer advantages of low cost, excellent film-forming ability, and good environmental compatibility [7–9]. However, inherent drawbacks including poor water resistance, insufficient adhesion, and limited barrier performance lead to premature failure under prolonged corrosive media (e.g., Cl^-) penetration, restricting their high-demand applications [10]. To address these limitations, researchers have explored optimization strategies such as chemical modification and physical compounding to enhance their comprehensive anticorrosive properties [11,12].

In the field of self-crosslinking acrylic latexes, a variety of internal crosslinking strategies have been developed to improve film performance, emerging as a core direction for boosting the overall capabilities of waterborne acrylic coatings. Parvate et al. [13] systematically elaborated on the application of N-methylolacrylamide (NMA) as a classic self-crosslinking monomer in their review, noting that it can form a three-dimensional network through self-condensation reactions, significantly enhancing the hardness, water resistance, and solvent resistance of the film. However, the review also clearly points out that self-crosslinking systems are prone to pre-crosslinking during storage, leading to reduced emulsion stability, and excessively high crosslinking density tends to increase film brittleness, compromising protective reliability in dynamic service environments. Beyond NMA systems, glycidyl methacrylate (GMA) has also been widely used in the preparation of self-crosslinking acrylic latexes due to the high reactivity of its epoxy groups [14–16]. For instance, Qin et al. [17] constructed coatings with both high hardness and good adhesion through ring-opening crosslinking reactions between GMA and carboxyl monomers. Nevertheless, the hydrophilicity of epoxy groups limits the improvement in coating water resistance, and the difficulty in precisely regulating crosslinking reaction rates often results in localized over-crosslinking.

Li et al. [18] developed fluorine-containing cationic self-crosslinking emulsions with enhanced stability and film formation; fluorinated segments reduced surface energy and improved hydrophobicity and anti-fouling performance. However, high cost and environmental concerns limited large-scale application. Similarly, Chen et al. [19] prepared silicone-modified self-crosslinking emulsions with improved temperature resistance and weatherability, but silane hydrolysis easily induced gelation and interfacial incompatibility led to microdefects. Parsimehr et al. [20] investigated the DAAM–ADH crosslinking system and revealed the combined effects of crosslinking density and T_g on mechanical properties. Modulating the DAAM/ADH ratio allowed tuning of modulus and elongation, but excessive crosslinking reduced toughness and humidity sensitivity caused film defects. Maleimide-based crosslinkers have also been explored [21–24]; Ehrhardt et al. [25] achieved thermally crosslinked coatings with high stability, but high reactivity risked polymerization runaway and high synthesis costs restricted industrialization.

In the realm of chlorinated rubber (CR) anticorrosive coatings, Sakhri et al. [26] confirmed that CR can effectively block the penetration of corrosive media by virtue of its excellent hydrophobic barrier effect. However, traditional CR coatings rely on organic solvents such as toluene and xylene for dissolution, resulting in high VOC emissions and posing severe challenges to environmental compliance. Emira et al. [27] enhanced the protective performance of coatings by incorporating active rust-inhibiting pigments (e.g., zinc phosphate) into chlorinated rubber (CR). However, the interfacial compatibility between CR and waterborne resin systems remains an unaddressed challenge, which may result in phase separation and compromised adhesion in the composite coatings. Thus, how to integrate the film-forming advantages of waterborne self-crosslinking acrylic latexes with the barrier properties of CR, while avoiding their respective drawbacks—including emulsion storage stability, film brittleness, high VOC emissions, environmental compliance, and interfacial compatibility—has become a critical bottleneck in current research.

Although some studies have attempted to compound these two components, systematic research on the evolution of their microstructure, interfacial interaction mechanisms, and long-term anticorrosive behavior remains insufficient. For example, the introduction of crosslinking monomers (e.g., N-methylolacrylamide, NMA) can form a three-dimensional network structure, enhancing coating compactness and mechanical strength. As a traditional anticorrosive material, CR's hydrophobicity and the barrier effect provided by chloride ions have been widely utilized in solvent-borne systems, but research on waterborne chlorinated rubber (WCR) remains relatively underdeveloped. While existing works have attempted to compound acrylic resin with CR, most focus on simple blending, lacking systematic research on the synergistic regulation of crosslinking degree and compounding ratio. The main existing deficiencies are reflected in three aspects: first, the mechanism by which the dosage of crosslinking monomers affects coating microstructure is unclear, and excessive crosslinking may lead to increased brittleness; second, the compatibility and interfacial interactions between CR and acrylic resin have rarely been explored in depth, resulting in an incomplete understanding of the long-term anticorrosive mechanism of composite systems; third, most studies ignore the correlation between wet adhesion and corrosion inhibition, leading to poor wet adhesion of coatings and easy debonding in humid environments.

To address the aforementioned shortcomings, this study proposes an innovative strategy: designing and synthesizing NMA/2-hydroxyethyl acrylate (HEA) crosslinked acrylic latex (N-HAR-X), and utilizing the cavities of the self-crosslinking latex to effectively adsorb waterborne chlorinated rubber (WCR), forming stable composite latex particles. This strategy aims to leverage the synergistic effect of the compactness of the crosslinked network and the hydrophobicity of CR to inhibit the penetration of corrosive media, while enhancing the wet adhesion between the coating and the metal substrate. This paper first reviews the development status of waterborne anticorrosive coatings to clarify research gaps; it then elaborates on the synthesis mechanism of crosslinked polymers and the compounding process in detail, and systematically evaluates the structure, mechanical properties, and long-term anticorrosive performance of composite coatings through multi-scale characterization techniques (such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS)). Ultimately, this study provides a theoretical basis and practical pathway for the development of high-performance waterborne anticorrosive coatings.

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA, chemically pure), styrene (St, chemically pure), 2-ethylhexyl acrylate (2-EHA, chemically pure), 2-hydroxyethyl acrylate (HEA, chemically pure), and Methacrylic acid (MAA, chemically pure) were purchased from Jiangsu Qiangsheng Functional Chemicals Co., Ltd. N-Methylolacrylamide (NMA, analytical reagent) and 2-hydroxyethyl acrylate (HEA, analytical reagent) were supplied by Macklin Biochemical Co., Ltd. (Shanghai). Ammonium persulfate (APS, analytical reagent) was obtained from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Aqueous chlorinated rubber (WCR) was sourced from Ningbo Haoxin Yulong New Material Co., Ltd., while the anionic emulsifier FES32 and nonionic emulsifier S90 were provided by BASF (China) Co., Ltd. and Sasol Chemicals (Shanghai) Co., Ltd., respectively. In addition, texanol as the film-forming aid (purchased from Macklin) and sodium nitrite (NaNO_2 , analytical reagent) serving as the flash rust inhibitor were acquired from commercial suppliers.

2.2. The process for the preparation and coating of N-HAR-X/WCR-Y composite latexes

The study employed a stepwise variable-control approach to

investigate how the self-crosslinking structure and chlorinated rubber (CR) content influence the morphology and properties of composite coatings.

At first, the self-crosslinkable acrylate latex was designed and used as the vesicles of composite dispersion via effective compounding of basic monomers (MMA, St, 2-EHA) and functional monomers (NMA, HEA). The glass transition temperature (T_g) of the as-prepared self-crosslinking acrylate latex polymer was regulated to 40 °C calculated according to FOX formula. Deionized water was used as the dispersion medium, the emulsification system consisted of anionic emulsifier (FES32) and nonionic emulsifier (S90), and ammonium persulfate (APS) was adopted as the aqueous free-radical initiator in the initiation system. The detailed formulations mentioned above are listed in Table S1 of the supporting information, and the above pre-emulsion was polymerized via a semi-continuous emulsion polymerization method, ultimately yielding a self-crosslinkable acrylate latex.

Then, the synthesized self-crosslinkable acrylic latex was maintained at 60 °C, a temperature above its T_g value, to ensure adequate particle flexibility for subsequent compositing. Different mass ratios of an aqueous chlorinated rubber dispersion were then added sequentially. During stirring, the hydrophobic CR segments migrated into the acrylic latex particles, driven by the core-shell structure of the latex (hydrophilic surface, hydrophobic interior). This process yielded a structurally stable composite latex, which are named as N-HAR-X/WCR-Y, X denotes the relative content of the crosslinkable monomer NMA with respect to the acrylic latex, while Y represents the addition amount of WCR relative to the composite latex. To systematically investigate the factors influencing the properties of the composite latexes, the experimental design consisted of two stages:

Stage 1: The CR content was fixed at 20 wt% (relative to the total mass), while the amount of N-hydroxymethylacrylamide (NMA) functional monomer was varied relative to the acrylic latex at 0, 0.5, 1, 1.5, and 2 wt%. This series examined the effect of the degree of self-crosslinking.

Stage 2: The NMA content was fixed at 1.5 wt% (relative to the acrylic resin), and the total CR content was varied at 5, 10, 15, 20, 35, and 50 wt% to evaluate the impact of CR concentration on coating morphology and performance.

At last, the obtained composite latexes were coated onto two types of

substrates, namely steel panels and silica glass slides, and the detailed painting process is described in the Supporting Information. The step-wise curing protocol help minimize coating defects and promoted sufficient resin crosslinking, ultimately producing N-HAR-X/WCR-Y composite coatings with a dense structure and stable performance for subsequent characterization. The synthesis process and the followed self-crosslinking curing reaction process is illustrated in Fig. 1 and the complete molecular structural evolution diagram of latex synthesis, WCR encapsulation and thermal curing is provided in Fig. S1.

2.3. Characterizations

Fourier transform infrared (FTIR) spectra of the samples were obtained using a Nicolet iS50 Fourier transform infrared spectrometer (Thermo Fisher Scientific, USA). Gel fraction measurement: Approximately 1.0 g (W_0) of the emulsion was dried at 140 °C to a constant weight to obtain a solid film. The film was then subjected to Soxhlet extraction with tetrahydrofuran (THF) at 80 °C for 24 h. The insoluble residue was dried in a vacuum oven at 80 °C to a constant weight (W_1). The gel fraction was calculated using the formula: Gel fraction (%) = $(W_1 / W_0) \times 100\%$. Each sample was measured in triplicate and the average value was reported. DSC analysis was carried out by the Diamond DSC 8000 Differential Scanning Calorimeter apparatus, and the heating&cooling cycles were conducted between -50 °C and 100 °C at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen. The thermal stability of the coatings was analyzed by a Diamond TG-DTA thermogravimetric analyzer Perkin Elmer Instruments. To study the mechanical properties of the coatings, various testing instruments were employed. The toughness of the coatings was evaluated using a QTY-32 type paint film bending tester according to GB/T 1731-2020. The impact resistance of the coatings was tested using a BGD 302 tubular paint film impactor according to GB/T 20,624.2-2006. The hardness of the coatings was assessed by the pencil hardness method according to GB/T 6739-2006. The Wear resistance tests of the coatings was conducted using JM-V rotate the friction rubber wheel according to ISO 7784-2:1997. Contact angle measurements were performed using a Theta Lite Contact Angle Meter from Biolin Scientific with distilled water ($\gamma = 72.8$ mN/m; $\gamma_d = 21.8$ mN/m; $\gamma_p = 51$ mN/m). The surface and cross-sectional morphologies of the cured composite coatings based on N-HAR-X/WCR-Y were analyzed using scanning electron microscopy (SEM) with the SEM4000 (CIQTEK Co., Ltd). The morphology of the

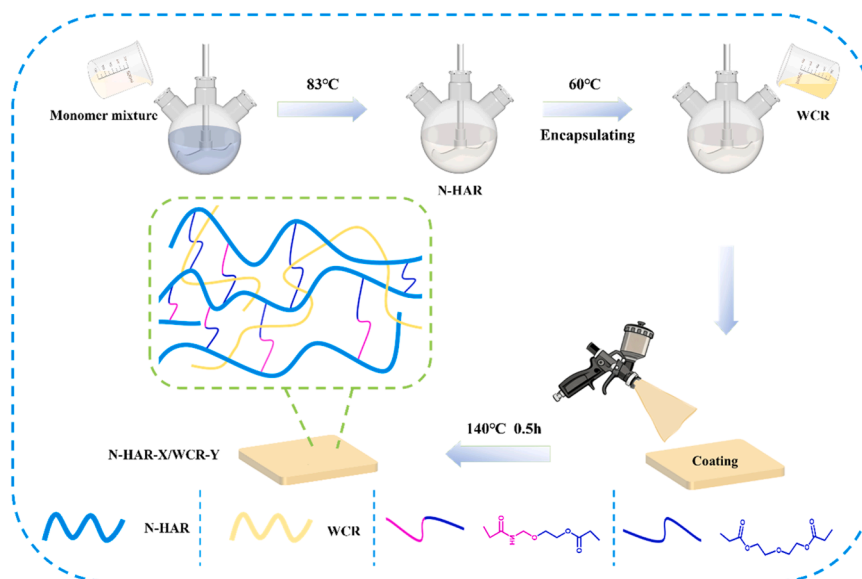


Fig. 1. Schematic of N-HAR synthesis (83 °C), WCR encapsulation (60 °C), N-HAR-X/WCR-Y composite formation, coating spraying, and curing (140 °C, 0.5 h), with component molecular structures.

latex particles was observed using transmission electron microscopy (TEM) on a Tecnai 12 instrument (Philips, Netherlands) operating at an accelerating voltage of 120 kV. Prior to observation, the latex samples were diluted with deionized water to an appropriate concentration, and a drop of the diluted dispersion was placed on a carbon-coated copper grid and dried at room temperature. The corrosion resistance of the coatings was investigated using a CHI660A electrochemical workstation by analyzing AC impedance. This involved immersing the cured coatings in a 3.5 wt% NaCl solution, with the coated steel plate serving as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The coating test area was 9.6 cm².

3. Results and discussion

3.1. Study on the structure and intrinsic properties of composite latex

Firstly, FTIR spectroscopy provides direct molecular-level evidence for the structural evolution of N-HAR during NMA incorporation and thermally induced crosslinking. As shown in Fig. 2, the –OH stretching vibration near 3400 cm^{−1} exhibits distinct responses to reaction progression: in N-HAR-0 (without NMA), a moderately broad peak arises solely from HEA. In contrast, uncrosslinked N-HAR-1 (cured at 80 °C) displays a significantly intensified and broadened –OH band, attributable to the combined presence of HEA's –OH and NMA's hydroxymethyl (–CH₂OH) groups—yet no condensation occurs at this stage, as evidenced by the absence of peak attenuation. Upon heating to 140 °C, however, the –OH signal is markedly suppressed, directly confirming intermolecular etherification between hydroxymethyl and hydroxyl functionalities, which consumes free –OH groups and establishes covalent crosslinks. Concurrently, the ester carbonyl stretching vibration at ~1730 cm^{−1} remains invariant across all samples, underscoring the chemical stability of the acrylic backbone and its insensitivity to both NMA grafting and network formation. The emergence of the amide II bending mode at ~1540 cm^{−1}—absent in N-HAR-0 but clearly present in both thermal states of N-HAR-1—serves as a definitive marker of successful NMA incorporation via vinyl copolymerization; its persistence after curing further indicates the robustness of the amide moiety under crosslinking conditions. Most critically, the C–O–C stretching band at ~1131 cm^{−1} intensifies dramatically post-curing, a result of

superposition between pre-existing ester linkages and newly formed ether crosslinks, thereby offering compelling spectral validation of three-dimensional network construction. Together, these FTIR features—tracked through shifts in peak intensity, shape, and chemical context—not only corroborate the copolymerization of NMA into the acrylic matrix but also delineate the complete trajectory of crosslinking, bridging molecular transformations with macroscopic material development.

Then the factors influencing the molecular weight of self-crosslinkable latexes were investigated. Table S2 summarizes the molecular weight properties of the synthesized latexes as determined by GPC, along with their corresponding gel fractions measured via Soxhlet extraction. The pure acrylic latex (HAR, 0% NMA), obtained via linear copolymerization, showed the highest number-average ($M_n \approx 365,600$ g/mol) and weight-average ($M_w \approx 1323,000$ g/mol) molecular weights. Without cross-linking, maximal chain growth was enabled, resulting in a broad molecular weight distribution ($\bar{D} = 4.2$)—a characteristic feature of conventional free-radical polymerization. Incorporation of the difunctional monomer NMA—equipped with both a polymerizable vinyl group and a reactive hydroxymethyl group—markedly altered the polymerization kinetics and topological structure of the resulting copolymers. At low NMA contents (0.5–1.0 wt%), the vinyl group participated efficiently in radical copolymerization, yielding molecular weights (M_n , M_w) comparable to the pure acrylic system. Even at these low levels, however, pendant hydroxymethyl groups could undergo intermolecular or intramolecular condensation reactions in the later polymerization stages, inducing mild branching. This incipient chain structure heterogeneity kept the molecular weight distribution relatively broad (e.g., $\bar{D} = 3.83$ for N-HAR-0.5). An optimal NMA content of 1.5 wt% (N-HAR-1.5) produced the most uniform polymer structure. At this concentration, an appropriate cross-linking site density was achieved. During and post-polymerization, hydroxymethyl groups efficiently formed ether or methylene bridges between chains, constructing a homogeneous three-dimensional network. This network balanced the growth of different polymer chains, establishing a kinetic equilibrium between propagation and cross-linking. Consequently, the molecular weight distribution narrowed sharply ($\bar{D} = 1.36$), and the gel fraction peaked at 0.061%—confirming the formation of a well-developed, uniform network. In contrast, increasing NMA content further to 2.0 wt% (N-HAR-2) exerted detrimental effects. Excessively high cross-linking density promoted premature formation of localized microgels in the early polymerization stages. These microgel domains trapped active radical centers, severely impeding the diffusion of monomers and radicals—a phenomenon termed the "diffusion-controlled effect" or "self-inhibition." This restriction on chain propagation drastically reduced both M_n (~88,800 g/mol) and M_w (~176,300 g/mol). Increased spatial heterogeneity of the reaction system—with overcrosslinked regions coexisting with under-reacted areas—broadened the molecular weight distribution again ($\bar{D} = 1.95$). Additionally, premature immobilization of cross-linking reactions within confined microgel regions led to a substantial drop in the macroscopic gel fraction to 0.01%. In summary, NMA content critically regulates the competition and balance between its copolymerization and cross-linking functionalities. This balance enables precise tuning of polymerization kinetics, polymer topological architecture, and ultimately, molecular weight, molecular weight distribution, and gel content.

Subsequently, the key influencing factors governing the particle size and Zeta potential of the as-prepared composite polymer latexes were systematically investigated. First, for the synthesized self-crosslinking latex, analysis results from Fig. 3(a) and (c) revealed that the introduction of NMA comonomer induced no obvious variation in the particle size of latex particles in comparison with pure acrylic latex. Nevertheless, the Zeta potential of latex particles exhibited a distinct regularity with the variation in NMA/HEA content. With the increase in NMA/HEA content from 0% to 1.5%, the absolute value of Zeta potential rose continuously from −29.37 mV to −37.80 mV, indicating a remarkable

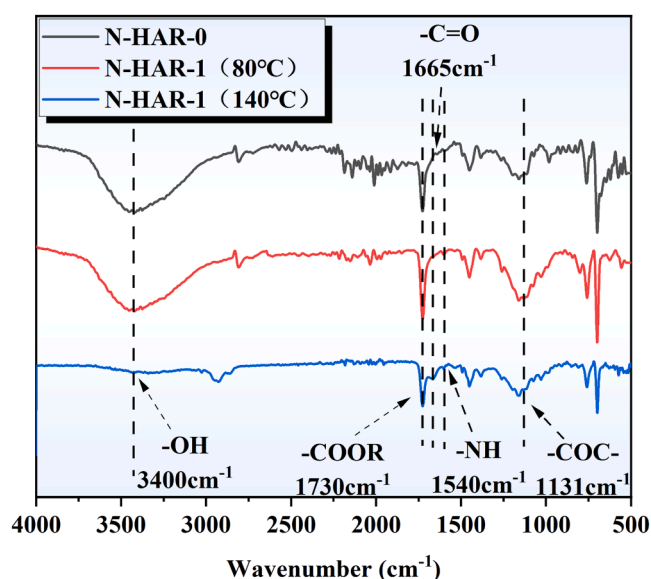


Fig. 2. FTIR spectra of N-HAR-0 and N-HAR-1 under different heat treatment temperatures (80 °C and 140 °C), displaying characteristic absorption peaks of functional groups (–OH, –COOR, C=O, –NH, and –COC–).

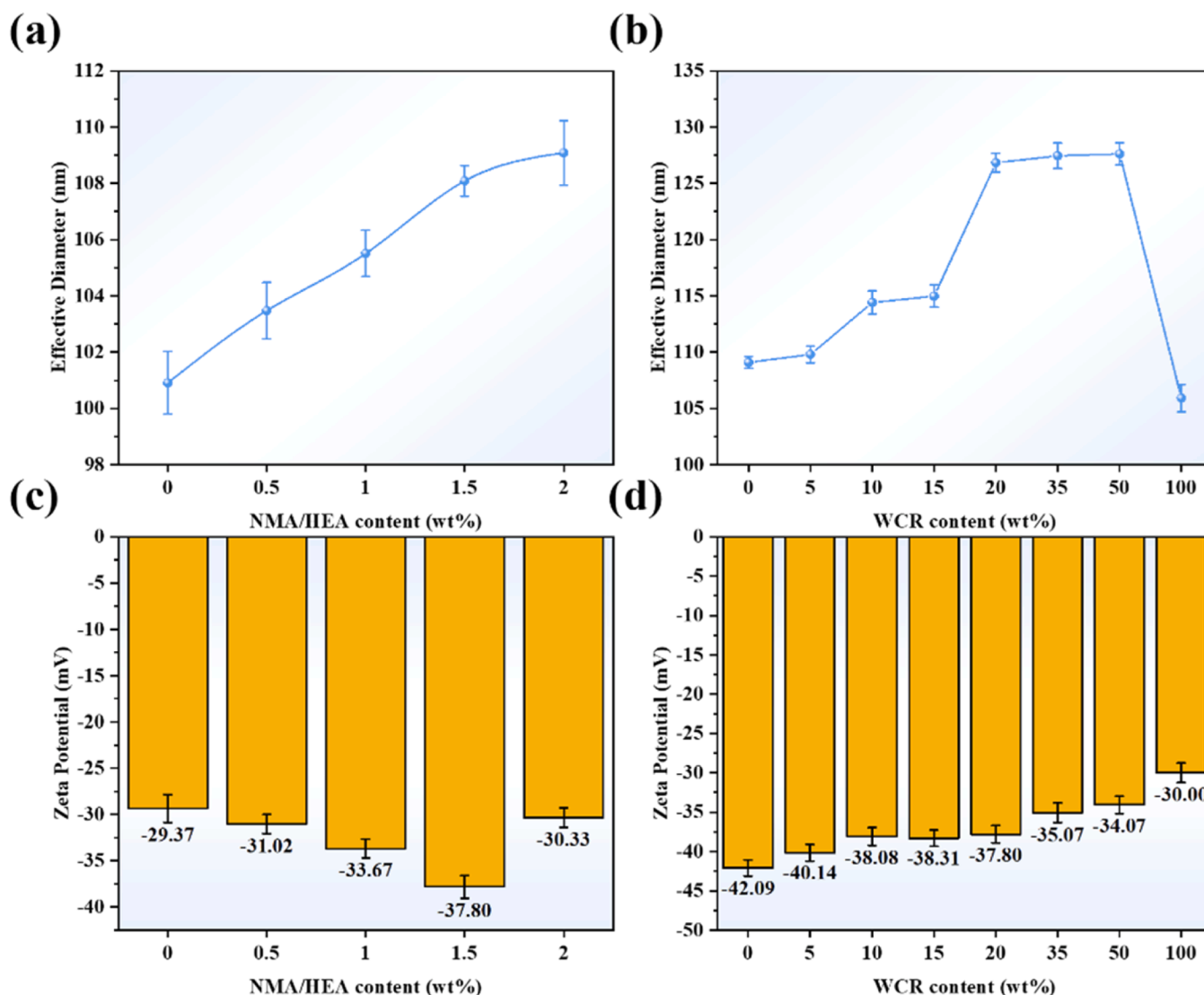


Fig. 3. (a) Particle size of the composite latex with different NMA/HEA contents. (b) Particle size of emulsion with varying chlorinated rubber content. (c) Zeta potential of emulsions with different NMA/HEA content. (d) Zeta potential of emulsions with different chlorinated rubber Concentrations.

enhancement in the negative charge density on the particle surface and a gradual optimization of the system's electrostatic stability. This phenomenon could be attributed to the preferential migration and accumulation of hydrophilic amide and hydroxymethyl groups in NMA molecules toward the particle-water interface during polymerization, which consequently enhanced the surface hydrophilicity and ionization capacity, and effectively improved the interfacial charge density and electrostatic double layer stability in the electrophoresis process. However, a further increase in NMA content to 2% led to a decrease in the absolute Zeta potential value to -30.33 mV, reflecting a decline in the colloidal stability of the latex system. Combined with the previous analysis on molecular weight and gel behavior, an excessively high NMA content was found to trigger the premature formation of local microgel structures in the reaction system, which induced the diffusion-controlled effect and potentially impaired the uniform distribution and effective ionization of functional groups on the particle surface, thereby weakening the stability of the surface potential.

The variation in Zeta potential was highly consistent with the structural evolution reflected by molecular weight distribution and gel fraction. This further confirmed that an appropriate NMA content (e.g., 1.5%) enabled an optimal synergy between molecular structure and colloidal stability, whereas an excessive NMA content would result in

deteriorated performance due to the increased structural inhomogeneity of the latex.

Based on the aforementioned findings, the N-HAR-1.5 latex with the optimal self-crosslinking structure was ultimately selected as the matrix to systematically investigate the adsorption and coating behaviors of aqueous chlorinated rubber (WCR) dispersions with different contents, along with their regulatory effects on the particle size and Zeta potential of the composite latex. As can be seen from the test results in Fig. 3(b) and (d), the hydrodynamic particle size of the composite latex shows a gradual increase with the rising WCR dosage. This phenomenon can be elucidated from the perspective of molecular interaction mechanisms: under the stabilization of emulsifiers, the hydrophobic WCR dispersed phase spontaneously forms micelles or fine particles in the aqueous phase. When the system is heated and stirred (reaction temperature > 60 °C), the acrylic latex particles soften owing to their glass transition temperature ($T_g \approx 40$ °C), which significantly enhances the mobility of molecular chains. At this stage, WCR, by virtue of its hydrophobicity and compatibility with the matrix, readily penetrates into the hydrophobic core layer of acrylic latex particles to achieve stable coating, ultimately leading to swelling-driven dimensional expansion of the composite particles. Regarding interfacial electrochemical properties, changes in Zeta potential further reveal the intrinsic stability mechanism of the

composite system. The Zeta potential of the WCR dispersion itself is approximately -30 mV; after its incorporation into the N-HAR-1.5 system, the absolute value of the Zeta potential of the composite latex decreases moderately. This variation indicates that the adsorption of WCR on the latex particle surface partially shields or neutralizes the negative charges generated by hydrophilic groups (e.g., $-\text{COOH}$, $-\text{OH}$) on the acrylic latex particles, thereby attenuating the electrostatic repulsion between particles. Notably, when the WCR dosage is in the intermediate range (e.g., 15–25 wt%), the growth of composite latex particle size remains controllable, and the Zeta potential can still maintain a relatively high absolute value (above ~ -35 mV), indicating no obvious aggregation or destabilization of the system. This implies that within this ratio range, besides the traditional electrostatic stabilization, the steric hindrance effect provided by emulsifiers and polymer chains begins to dominate, synergistically sustaining the kinetic stability of the composite emulsion.

Overall, WCR realizes effective combination with self-crosslinking acrylic latex via a hydrophobic adsorption-coating mechanism, and its dosage acts as a critical factor governing the size and surface potential of composite particles. At optimal mixing ratios, these two components can form a composite dispersion system with excellent compatibility and stability, which provides a vital structural foundation for the subsequent fabrication of dense composite coatings with superior comprehensive performance.

To further explore the microstructure and compatibility of the blending system consisting of NMA/HEA crosslinkable acrylic latex and aqueous chlorinated rubber (WCR), Transmission Electron Microscopy (TEM) was used for systematic morphological comparison of N-HAR-1.5 latex, WCR dispersion, and the resultant N-HAR-1.5/WCR-20 composite latex. As shown in Fig. 4, N-HAR-1.5 latex particles exhibit regular spherical morphology with uniform size distribution and distinct interfaces (Fig. 4(a)), indicating excellent monodispersity and structural integrity. In contrast, WCR forms nanoscale dispersed microspheres under emulsification (Fig. 4(b)), laying a structural foundation for subsequent compounding with acrylic latex. After blending, the composite latex particles retain an overall spherical shape but show a significant increase in particle size (Fig. 4(c)), with no signs of poor compatibility (e.g., phase separation, blurred interfaces, or local agglomeration) observed. This morphological evolution confirms that under heating and blending conditions, the hydrophobic WCR dispersed phase overcomes the interfacial energy barrier via its compatibility with the acrylic matrix, penetrating and embedding into the hydrophobic core of latex particles to achieve microscale structural integration. The preservation of the acrylic latex's spherical structure implies strong molecular chain-level affinity between the two components, which form a homogeneous, interface-stable composite latex system through hydrophobic interactions and potential local interpenetration. This intact spherical morphology and uniform dispersion provide a critical structural basis for the formation of dense, continuous composite coatings during film formation, while offering direct morphological evidence for the enhanced barrier and mechanical properties of the composite system.

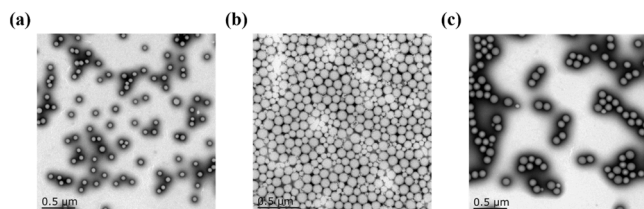


Fig. 4. TEM images of the latexes. (a) N-HAR-1.5 latexes. (b) WCR emulsion. (c) N-HAR-1.5/WCR-15 latexes.

3.2. Study on the morphology and performance of the cured coatings derived from N-HAR-X/WCR-Y composite latex

Building on the insights into the microstructural characteristics of the composite latexes, the following section focuses on the cured coatings fabricated from them, aiming to clarify the correlation between their morphological features and performance.

3.2.1. Surface and cross-sectional micromorphology of the composite coatings

Taking the N-HAR-1.5/WCR-15 composite system as an example, Fig. 5 shows the FESEM images of the coating's surface and cross-section. Morphological observations reveal an overall continuous, flat surface free of obvious defects (e.g., cracks, pinholes, local agglomeration), while the cross-section exhibits a uniform, dense structure without significant phase separation or pore formation.

The SEM images presented in Fig. 5 reveal a continuous, flat surface and a uniform, dense cross-sectional morphology for the N-HAR-1.5/WCR-15 composite coating. No visible defects—such as cracks, pinholes, or phase-separated domains—are observed, indicating excellent compatibility between the NMA/HEA-crosslinked acrylate matrix and the encapsulated WCR phase. This intact and defect-free microstructure provides a robust physical barrier that is expected to significantly prolong the diffusion pathways of corrosive species (e.g., H_2O , O_2 , and Cl^-), thereby enhancing the protective performance of the coating. It is reasonable to infer that such structural densification originates, at least in part, from the restricted mobility of polymer chains imposed by the NMA/HEA crosslinking network. Accordingly, the thermodynamic behavior of the coatings was examined in the subsequent section to validate this hypothesis.

3.2.2. Thermodynamic properties of the composite coatings

The glass transition temperature (T_g), the thermodynamic temperature at which polymer segments undergo micro-Brownian motion, exerts a decisive effect on the practical application and service scope of polymeric coatings. Herein, a single-factor variable approach was adopted, with the dosages of NMA/HEA crosslinking monomers and waterborne chlorinated rubber (WCR) fixed separately, to systematically investigate their regulatory effects on the thermodynamic properties of the composite coatings. As shown in Fig. 6(a), the T_g of the composite coatings increases significantly with the rising loading of NMA. In the crosslinked polymer system, acrylic macromolecular chains are interconnected via crosslinking sites to form a continuous three-dimensional network, which acts as physical anchors to strongly restrict the free sliding and mobility of polymer segments. For segmental motion to occur, the polymer chains must overcome the additional steric hindrance and constraints of the crosslinking network, leading to a marked increase in the required activation energy and thus an elevated T_g of the composite coatings.

The effect of linear chlorinated rubber loading on the T_g of this blend system is clearly illustrated in Fig. 6(b). With the increase in chlorinated rubber content in the system, the T_g of the composite coatings presents a monotonous decreasing trend, dropping gradually from a peak value of 42.40°C to 35.15°C , with a total decrease of $>6^\circ\text{C}$. When linear chlorinated rubber is blended with self-crosslinking acrylic resin, its molecules intercalate into the interstices of acrylic macromolecular chains. This not only increases the average distance between macromolecular chains but also induces a gradual reduction in the effective crosslinking density of the coatings, thus creating more abundant free volume for the movement of polymer segments. In this process, linear chlorinated rubber molecules act as a "molecular lubricant", which effectively facilitates the motion of acrylic segments in the blend system and thereby enables the glass transition to be initiated at a lower temperature.

The effects of the two variables on the thermal resistance of the composite coatings were further investigated, and the influence of NMA

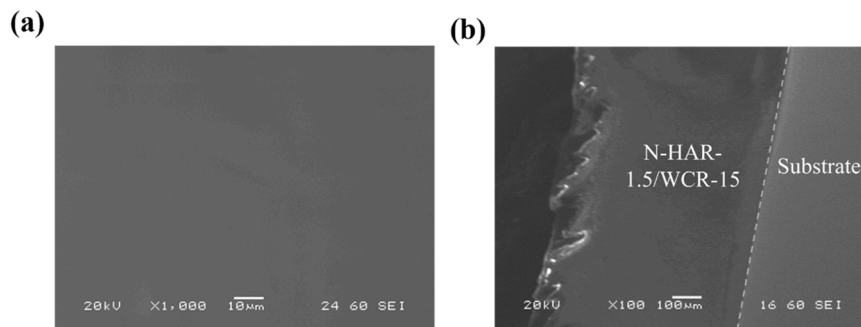


Fig. 5. SEM images of N-HAR-1.5/WCR-15: (a) Surface morphology; (b) Cross-sectional morphology.

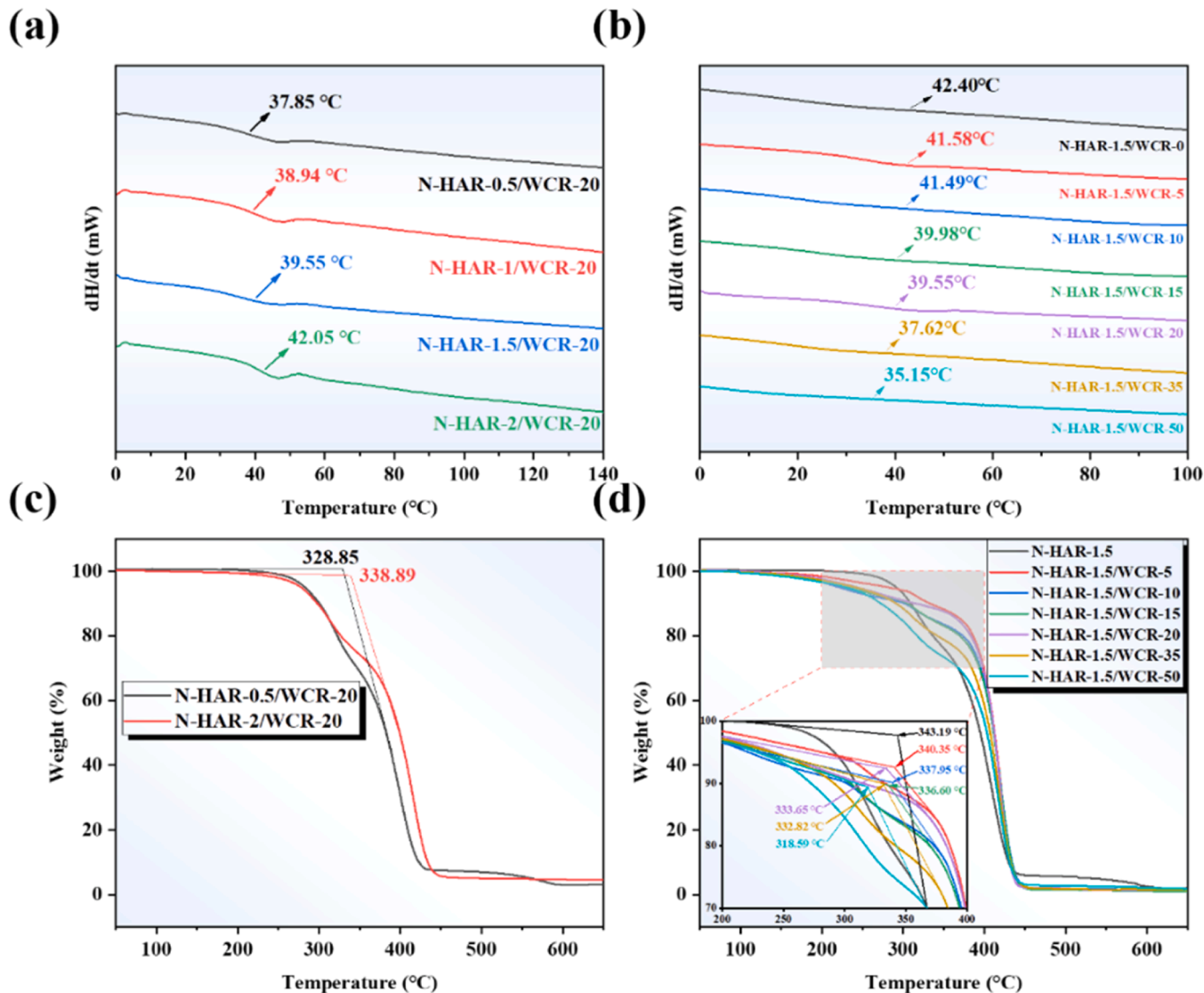


Fig. 6. DSC and TGA of N-HAR-X/WCR-Y coating. (a-b) Different NMA/HEA content. (c-d) Different chlorinated rubber content.

loading on the thermal stability of composite coatings with a fixed WCR content is distinctly depicted in Fig. 6(c). It can be observed that the thermal decomposition onset temperature and the residual weight of the composite coatings at the same temperature both increase progressively with the elevation of NMA content and the corresponding enhancement of crosslinking density. The increase in NMA loading constructs a more compact and integrated three-dimensional crosslinking network within

the coating system, which not only reinforces the inherent thermal stability of polymer molecular chains but also effectively suppresses the thermal motion and decomposition of chain segments, as well as reduces the escape rate of small molecules generated by thermal degradation. This result fully demonstrates that increasing the content of NMA crosslinking monomer to improve the crosslinking density of the coating is an effective approach to enhance the thermal resistance of the

composite coatings. The thermal decomposition process of the composite coatings exhibits a typical two-stage characteristic regardless of the variation in NMA content. The first stage occurs in the temperature range of 150–350 °C, where the mass loss is jointly caused by the dehydration of bound water in the samples, the thermal volatilization of a small amount of uncrosslinked low-molecular-weight oligomers in the system, and the preliminary pyrolysis of chlorine-containing functional groups in WCR. Specifically, the weak-bonded chlorine atoms on the WCR molecular chains break under thermal action and escape in the form of hydrogen chloride (HCl) small molecules, which constitutes an important contributor to the mass loss in this stage. When the temperature rises above 400 °C, a distinct thermal weight loss platform appears for the coatings, corresponding to the deep thermal degradation of the acrylic resin matrix. This stage involves multiple thermal decomposition reactions including the pyrolytic cleavage of ester groups, the decrosslinking of the three-dimensional network, and the random scission of C-C bonds in the polymer main chain, during which the polymer coatings undergo continuous thermal weight loss and gradual carbonization.

Distinct from the thermal weight loss behavior of pure acrylic resin coatings, the composite coatings with WCR incorporated exhibit an additional thermal weight loss characteristic in the range of 150–350 °C, and this trend becomes increasingly pronounced with the increase in WCR loading (Fig. 6(d)). This phenomenon directly confirms the thermal elimination of HCl from the chlorinated rubber component during the heating process. The pyrolysis of chlorinated rubber and the subsequent escape of HCl not only exert a negative impact on the thermal stability of the composite coatings but also serve as a key factor limiting the addition amount of chlorinated rubber in this blend system.

3.2.3. Mechanical properties and dry/wet adhesion of the composite coatings

The mechanical properties of coatings serve as a fundamental criterion for assessing their ability to withstand external mechanical stress in engineering applications. This study clarifies the synergistic regulatory mechanism of NMA/HEA crosslinking monomer content and waterborne chlorinated rubber (WCR) blending ratio on the mechanical behavior of N-HAR-X/WCR-Y composite coatings by systematically varying these two parameters. As shown in Table 1, at a constant WCR content, coating hardness increases notably with higher NMA/HEA levels. This trend is due to the dense three-dimensional network formed

through NMA/HEA crosslinking, which restricts molecular chain mobility and thus enhances macroscopic rigidity. Meanwhile, the molecular polarity and interchain van der Waals forces of chlorinated rubber contribute to a distinct toughness–rigidity balance in the composite coatings. In contrast, with NMA fixed at 1.5 wt%, raising the WCR content slightly reduces hardness, whereas the polar linear polymer chains of WCR significantly improve coating flexibility and impact resistance.

Abrasion resistance, a key intrinsic property of coatings, is closely linked to the microstructure of the coating film. The coupling between chemical crosslinks from NMA/HEA and van der Waals interactions among chloride ions in chlorinated rubber plays a significant role in regulating abrasion resistance, which was evaluated through wear tests using mass loss as the metric. Specifically, at a fixed WCR content of 20 wt%, increasing the NMA/HEA ratio from 0 wt% to 2 wt% reduced the abrasion mass loss from 0.0614 g to 0.0204 g. This improvement stems from the structural integrity imparted by covalent crosslinks, which mitigates wear damage. When NMA/HEA was held at 1.5 wt% and WCR content varied from 0 to 50 wt%, abrasion resistance first increased and then decreased, reaching an optimum (mass loss of 0.0198 g) at 15 wt% WCR. Excessive WCR dilutes the crosslinking monomer fraction and weakens network compactness, revealing a clear synergistic interaction between NMA/HEA and WCR.

Dry and wet adhesion are core indicators governing the long-term service stability of anticorrosive coatings, with their influencing factors varying distinctly with service environments. Dry adhesion, dominated by the coating-substrate interfacial interactions (hydrogen bonding, van der Waals forces, local chemical bonding), coating cohesive strength and polymer network crosslinking density, forms the basis for initial dry-state interfacial bonding, determines adhesion stability under conventional mechanical stress post-construction, and is an essential prerequisite for engineering application. Wet adhesion, by contrast, is built on dry adhesion and further regulated by coating hydrophobicity, corrosive medium impermeability, interfacial hydrophilic group distribution and action, and the coating's resistance to swelling and debonding in aqueous corrosive environments; it is critical for sustaining long-term interfacial bonding under humid, salt spray and immersion conditions, and directly dictates effective anticorrosive protection in harsh wet service scenarios (e.g., marine and chemical industries).

As shown in Fig. 7(a), at a fixed waterborne chlorinated rubber (WCR) content of 20 wt%, the dry adhesion of the composite coatings increased from 0.63 MPa to 1.11 MPa as the NMA/HEA content rose from 0 to 2 wt%. This improvement stems primarily from the increased crosslinking density, which not only enhanced coating cohesion but also strengthened interfacial interactions (e.g., hydrophilic group-substrate bonding), thereby effectively reinforcing the overall interfacial adhesion. Concurrently, the wet adhesion after 60 days of immersion in 3.5 wt% NaCl solution improved significantly from 0 to 0.30 MPa. This result confirms that elevated crosslinking density effectively resists water-induced interfacial debonding, markedly improving bonding stability in saline environments. In contrast, Fig. 7(b) shows that at a fixed NMA/HEA content of 1.5 wt%, dry adhesion exhibited a parabolic trend with increasing WCR content, peaking at 1.28 MPa at 15 wt% WCR before slightly decreasing at 50 wt%. This behavior reflects WCR's dual role: moderate addition enhances substrate compatibility via its chlorinated structure, boosting adhesion; however, excess WCR causes phase separation and dilutes the crosslinking network, compromising cohesion. Notably, wet adhesion increased monotonically with WCR content, rising from 0 MPa (0 wt% WCR) to 0.35 MPa (50 wt% WCR). This demonstrates that WCR significantly enhances coating hydrophobicity and barrier properties, thus greatly improving interfacial retention under wet corrosive conditions such as salt spray.

All the above results indicate that the moderate balance regulation of crosslinking degree and WCR addition amount can not only ensure the initial adhesion performance of the coating in a dry environment, but

Table 1

Mechanical properties of N-HAR-X/WCR-Y coatings with different NMA/HEA and chlorinated rubber contents.

	Hardness	Flexibility (mm)	Impact Resistance (kg.cm)	Quality loss (g)
N-HAR-0	H	0.5	50	0.0614
N-HAR-0.5/WCR-20	2H	0.5	50	0.0233
N-HAR-1/WCR-20	2H	0.5	50	0.0250
N-HAR-1.5/WCR-20	2H	0.5	50	0.0219
N-HAR-2/WCR-20	3H	0.5	50	0.0204
N-HAR-1.5/WCR-0	2H	1	30	0.0382
N-HAR-1.5/WCR-5	2H	1	40	0.0256
N-HAR-1.5/WCR-10	2H	0.5	50	0.0224
N-HAR-1.5/WCR-15	2H	0.5	50	0.0198
N-HAR-1.5/WCR-20	2H	0.5	50	0.0219
N-HAR-1.5/WCR-35	H	0.5	50	0.0338
N-HAR-1.5/WCR-50	H	0.5	50	0.0345

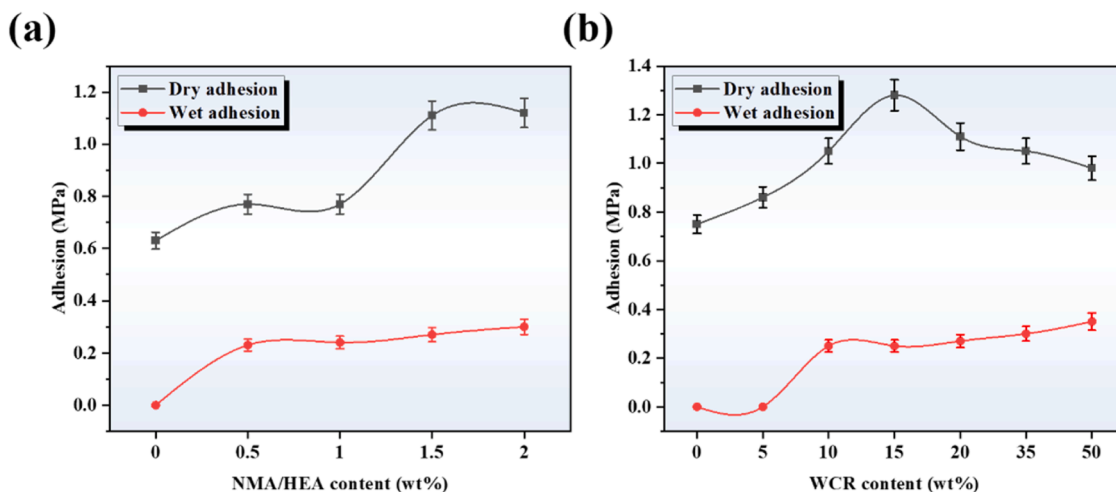


Fig. 7. Adhesion strength of N-HAR-X/WCR-Y composite coatings before and after corrosion exposure in 3.5 wt% NaCl solution for 60 days: (a) variation with NMA/HEA content (fixed WCR at 20 wt%); (b) variation with waterborne chlorinated rubber (WCR) content (fixed NMA/HEA at 1.5 wt%).

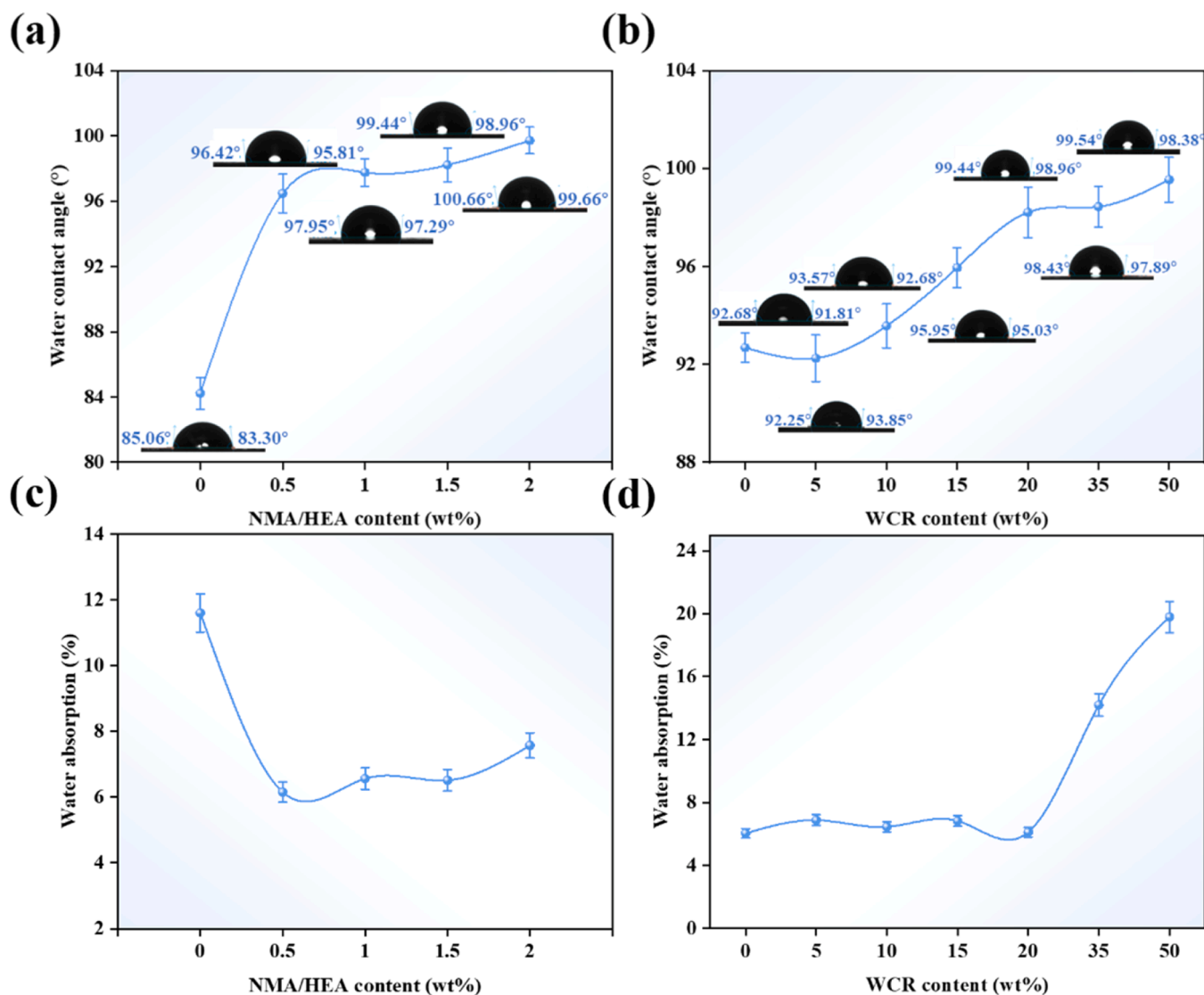


Fig. 8. (a) Water contact angle of N-HAR-X/WCR-Y coatings with varying NMA/HEA content. (b) Water contact angle of N-HAR-X/WCR-Y coatings with different chlorinated rubber content. (c) Water absorption of N-HAR-X/WCR-Y coatings with different NMA/HEA content. (d) Water absorption of N-HAR-X/WCR-Y coatings with different chlorinated rubber content.

also effectively improve its long-term interfacial stability under the action of corrosive media, which provides a crucial guarantee for the long-term service of the composite coating in harsh wet corrosion environments.

3.2.4. The surface wettability and water absorption behavior of the composite coatings

Surface wettability (evaluated by water contact angle) and water absorption are key indicators of coating anticorrosive performance, as they directly determine barrier properties toward corrosive media and interfacial stability [28,29].

With WCR content fixed, the water contact angle of the coatings increases significantly with rising NMA/HEA dosage (Fig. 8(a)). The NMA/HEA crosslinking system forms a compact three-dimensional network, which restricts polymer segment motion via spatial anchoring and suppresses the migration of hydrophilic segments to the surface, thus greatly improving hydrophobicity. All crosslinked samples exhibit water contact angles above 90° , which further increase with crosslinker content. At a fixed NMA/HEA content of 1.5 wt%, the water contact angle first increases and then stabilizes with increasing WCR content (Fig. 8(b)). As WCR rises from 0 to 15 wt%, the contact angle increases from 84° to 95° due to surface enrichment of hydrophobic components. Above 15 wt%, the contact angle plateaus at approximately 95° , suggesting saturated hydrophobic group coverage; excessive WCR may cause local aggregation without further improving wettability.

Water absorption measurements (Fig. 8(c)) confirm that the NMA/HEA crosslinking network significantly reduces water uptake by extending the diffusion pathway of water molecules. However, excessive NMA/HEA (e.g., 2 wt%) leads to increased water absorption, which is ascribed to residual hydrophilic hydroxyl groups from unreacted HEA. For WCR (Fig. 8(d)), water absorption remains low and stable within 0–15 wt%, but exceeds 20 wt% disrupts the crosslinking network and reduces compactness, resulting in higher water absorption and deteriorated long-term corrosion resistance.

These results demonstrate the importance of synergistic balance between crosslinking density and WCR content. The NMA/HEA network governs coating compactness and structural stability, while WCR reinforces hydrophobicity via surface enrichment and interfacial energy regulation. Rational matching of the two components maximizes barrier performance and avoids structural defects, providing a reliable strategy for formulation optimization of high-performance composite coatings.

3.2.5. Corrosion resistance of N-HAR-X/WCR-Y composite coatings

Electrochemical impedance spectroscopy (EIS) is a non-destructive and sensitive technique for evaluating the dynamic corrosion protection behavior of organic coating/metal systems [30–33]. It enables quantitative characterization of the evolution of coating 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 effects of NMA/HEA crosslinking degree and WCR content on the corrosion resistance of N-HAR-X/WCR-Y composite coatings. First, the relative addition amount of WCR was fixed to analyze the influence of the system's crosslinking density on the corrosion resistance of the coating. The tests were conducted in a simulated corrosive environment (3.5 wt% NaCl solution) for 60 days, with uncrosslinked acrylic resin coatings (N-HAR-0) as references (see in Fig. 9).

a. Nyquist plot analysis: evolution of coating barrier integrity

Nyquist plots illustrate the complex impedance response of coating/metal systems, reflecting the relationship between the real impedance (Z') and imaginary part ($-Z''$). The radius of the capacitive arc directly reflects the coating resistance (R_c), which determines the ability to suppress the penetration of corrosive species such as H_2O and Cl^- . A larger arc radius indicates a more compact microstructure and stronger barrier performance [34,35].

At the initial immersion stage (Day 1), all coatings displayed a single capacitive arc with impedance above $10^9 \Omega \cdot cm^2$ (Fig. 9(1a) and (2a)), suggesting an intact barrier structure. The initial coating resistances were high (N-HAR-0: $\sim 1.2 \times 10^9 \Omega \cdot cm^2$; pure WCR: $\sim 1.1 \times 10^9 \Omega \cdot cm^2$; N-HAR-1.5/WCR-15: $\sim 6.0 \times 10^9 \Omega \cdot cm^2$) with low capacitance ($C_c < 10^{-10} F \cdot cm^{-2}$), confirming dense and defect-free microstructures. The composite coatings exhibited larger arc radii than the control samples, owing to the synergistic barrier effect: The crosslinking network improves coating compactness by reducing free volume and restricting polymer chain mobility, while the hydrophobic WCR segments, via the strong van der Waals interactions between the chlorine atoms in their polymer chains, further densify the microstructure, reduce surface wettability and optimize the packing of the polymer matrix. Together, they create a highly tortuous diffusion pathway that effectively impedes the initial ingress of corrosive electrolytes.

After 5 days of immersion, the capacitive arc radii of all coatings decreased to varying degrees. N-HAR-0 showed a sharp drop to below $10^6 \Omega \cdot cm^2$, indicating complete barrier failure due to the lack of a crosslinking network. In contrast, pure WCR and N-HAR-X/WCR-Y composites maintained high resistance with only a one-order reduction.

At Day 45, N-HAR-0 exhibited a second capacitive arc ($Z' < 10^5 \Omega \cdot cm^2$), demonstrating that corrosive media had reached the metal interface and triggered corrosion. Pure WCR and N-HAR-2/WCR-20 showed a further one-order decrease in impedance. The degradation of pure WCR was caused by swelling of its linear structure, while the excessive NMA in N-HAR-2/WCR-20 left hydrophilic hydroxyl groups from unreacted HEA, weakening the barrier effect.

After 60 days of long-term immersion, N-HAR-0 almost lost its barrier property ($Z' < 10^4 \Omega \cdot cm^2$). This near-complete loss of barrier property is attributed to the inherent vulnerability of its linear polymer structure. Without a crosslinked network, the coating underwent significant swelling and micro-pore formation under prolonged electrolyte exposure, creating continuous conductive pathways that allowed corrosive species to reach the metal interface unimpeded. In contrast, N-HAR-0.5/WCR-20, N-HAR-1/WCR-20, and N-HAR-1.5/WCR-20 still maintained large capacitive arcs ($Z' > 10^8 \Omega \cdot cm^2$). This exceptional long-term stability is a direct consequence of its optimally constructed physical barrier. The moderate NMA content formed a uniform and complete three-dimensional crosslinked network that effectively suppressed polymer chain mobility and resisted swelling-induced structural degradation. Simultaneously, the well-dispersed WCR enhanced the overall hydrophobicity of the matrix and, due to its good compatibility with the acrylic phase, contributed to a denser, defect-free microstructure without causing phase separation. This synergistic combination of covalent crosslinking and hydrophobic modification created a highly tortuous diffusion path for corrosive media, effectively isolating the metal substrate from the electrolyte throughout the 60-day immersion period.

b. Bode magnitude plot analysis: quantitative evaluation of long-term protection

Bode magnitude plots ($\log|Z|$ vs. $\log f$) enable quantitative analysis of the dynamic evolution of coating protective performance, with the low-frequency impedance modulus ($|Z|_{0.01} Hz$) serving as a key metric for evaluating long-term corrosion resistance. Unlike mid-high frequency impedance that reflects bulk coating properties, $|Z|_{0.01} Hz$ directly correlates with the resistance to interfacial electrochemical reactions—higher values indicate stronger inhibition of corrosion kinetics, as they represent increased resistance to charge transfer and mass transport at the metal/coating interface [36,37].

At initial immersion (Day 1), all coatings exhibited $|Z|_{0.01} Hz$ above $10^{10} \Omega \cdot cm^2$, verifying intact initial barrier properties. N-HAR-1.5/WCR-15 showed the highest modulus ($\sim 1.2 \times 10^{11} \Omega \cdot cm^2$), an order of magnitude higher than N-HAR-0 ($\sim 1.5 \times 10^{10} \Omega \cdot cm^2$) and pure WCR ($\sim 1.1 \times 10^{10} \Omega \cdot cm^2$). This significant enhancement directly confirms the synergistic effect of NMA/HEA crosslinking and WCR modification in constructing a superior physical barrier that effectively impedes the

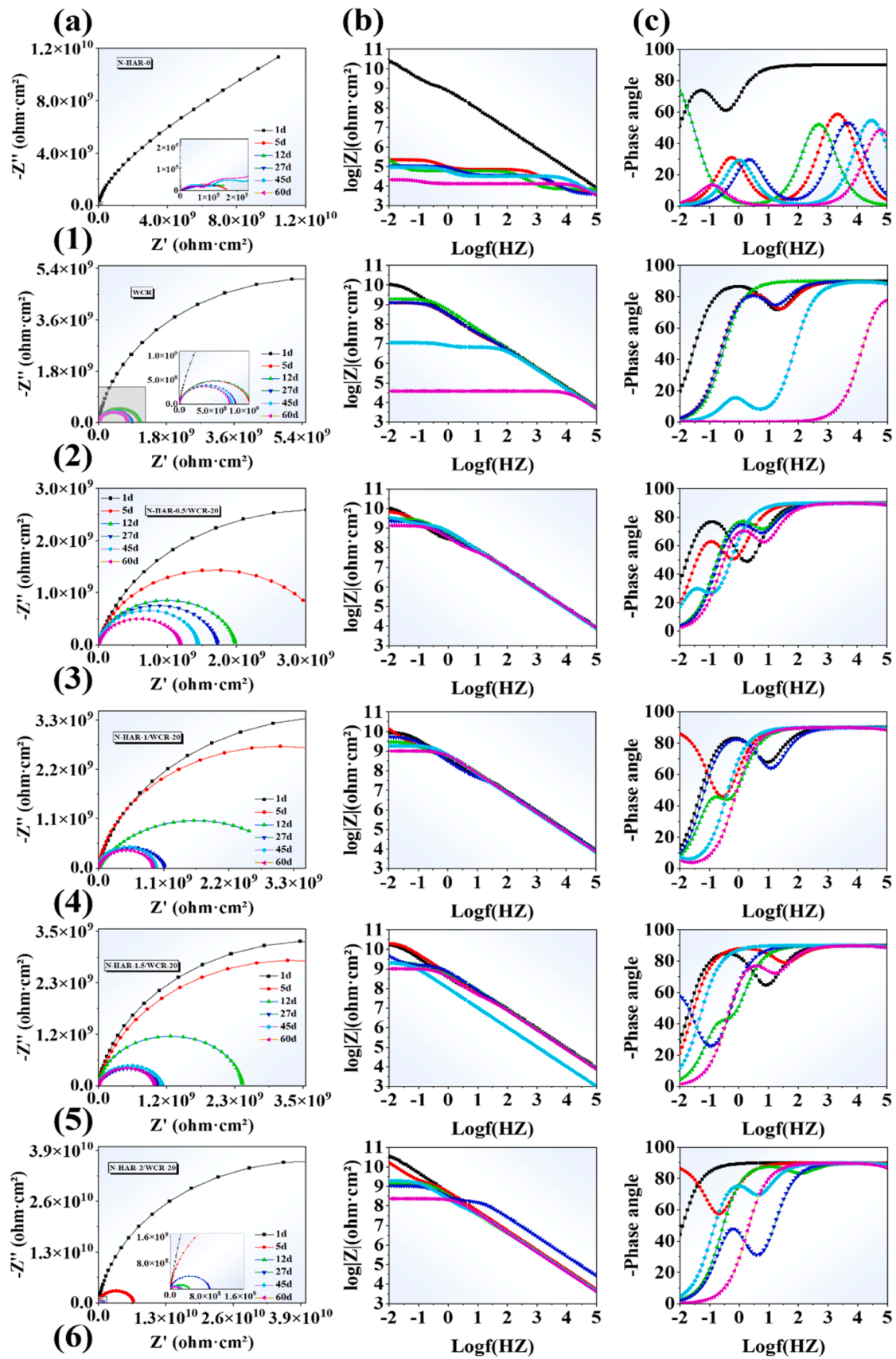


Fig. 9. Evolution of electrochemical impedance behavior for N-HAR-X/WCR-Y composite coatings during prolonged corrosion exposure. (a) Nyquist. (b) Bode magnitude. (c) Bode phase angle representations. (1) N-HAR-0; (2) WCR; (3) N-HAR-0.5/WCR-20; (4) N-HAR-1/WCR-20; (5) N-HAR-1.5/WCR-20; (6) N-HAR-2/WCR-20.

initial ingress of corrosive electrolytes.

Distinct degradation trends were observed across formulations over the 60-day immersion. N-HAR-0 exhibited a drastic decline in $|Z|_{0.01}$ Hz, plummeting to $\sim 10^6 \Omega\cdot\text{cm}^2$ by Day 5 and below $10^4 \Omega\cdot\text{cm}^2$ by Day 60. This rapid failure stems from the inherent vulnerability of its uncrosslinked linear structure, which cannot impede corrosive media penetration, leading to rapid interfacial delamination and loss of protective function. Pure WCR showed a gradual modulus decrease to $\sim 3.71 \times 10^7 \Omega\cdot\text{cm}^2$ after 60 days, revealing the limitations of sole hydrophobicity for long-term protection—its linear chains cannot resist swelling-induced structural damage without crosslinking.

In contrast, all N-HAR-X/WCR-Y composite coatings maintained $|Z|_{0.01}$ Hz above $10^9 \Omega\cdot\text{cm}^2$ throughout immersion, with N-HAR-1.5/WCR-15 showing the slowest degradation (remaining above $10^{10} \Omega\cdot\text{cm}^2$ after 60 days, Fig. 9(b)). Notably, N-HAR-1.5 (without WCR) saw a sharp $|Z|_{0.01}$ Hz drop to $\sim 3.71 \times 10^5 \Omega\cdot\text{cm}^2$ by Day 60, confirming that the incorporation of WCR is essential for achieving optimal long-term barrier performance by providing additional hydrophobic reinforcement to the crosslinked network.

c. Bode phase angle plot analysis: insight into coating capacitive behavior and ion diffusion

Bode phase angle plots (θ vs. $\log f$) characterize the electrochemical properties of the coating/metal system, with phase angle variations reflecting the relative contributions of capacitive and resistive components to the total impedance. A broad plateau near -90° denotes a compact, low-defect coating with robust capacitive and barrier performance, while plateau splitting or a sharp phase angle drop indicates coating degradation and the initiation of interfacial corrosion reactions [38,39].

At initial immersion, all coatings presented a wide -90° phase angle plateau (Fig. 9(1c) and (2c)), signifying intact barrier function and effective capacitive behavior. N-HAR-1.5/WCR-15 had the broadest plateau (10^2 – 10^4 Hz) compared with N-HAR-0 and pure WCR (10^1 – 10^4 Hz), which was attributed to its denser, more uniform microstructure-crosslinking and WCR modification synergistically reduced microvoids, minimized corrosive medium diffusion paths, and enhanced capacitive behavior. With extended immersion, phase angle evolution differed significantly between reference and composite coatings. In the high-frequency region ($>10^3$ Hz), all coatings retained phase angles near -90° , indicating intact outer surfaces and stable capacitive behavior at the coating/electrolyte interface. In the mid-frequency range (10^2 – 10^3 Hz), N-HAR-0 showed a sharp phase angle drop from -90° to $\sim -45^\circ$ by Day 5, caused by accelerated interfacial charge transfer (CT) processes. By contrast, N-HAR-X/WCR-Y composites, especially N-HAR-1.5/WCR-15, exhibited a gentle transition, stabilizing at -60° – -45° even after 60 days. This slow degradation is a direct consequence of the robust physical barrier provided by the crosslinked network, which effectively hinders ion transport and delays electrolyte penetration. The well-dispersed WCR phase further enhances this effect by increasing the tortuosity of diffusion paths and reducing water uptake. In the low-frequency region ($<10^2$ Hz), N-HAR-0's phase angle neared 0° at Day 60, showing pure resistive behavior and complete loss of capacitive characteristics. Pure WCR's phase angle dropped to -77° with the plateau disappearing, meaning corrosion reactions dominated and its barrier function was negligible. Remarkably, N-HAR-1.5/WCR-15 maintained phase angles above -45° with a flattened plateau still discernible, confirming that ion diffusion remained limited and capacitive behavior was largely preserved. This exceptional stability arises from the synergistic physical barrier created by the dense crosslinking network and the hydrophobic WCR phase, which together prolong the diffusion pathways of corrosive species and maintain coating integrity throughout prolonged exposure.

To further elucidate the role of WCR content in the composite coating system, the crosslinking density of the acrylic latex was fixed (NMA/HEA content at 1.5 wt%) and the relative addition amount of WCR was varied from 5 to 50 wt%. The electrochemical impedance evolution over

60 days of immersion in 3.5 wt% NaCl solution is presented in Fig. 10, with the impedance response following distinct patterns governed by the synergistic interplay between the crosslinking network and the hydrophobic WCR phase in constructing an effective physical barrier.

a. Nyquist plot evolution

At the initial immersion stage (Day 1, Fig. 10a), all composite coatings exhibited large capacitive arcs with real impedance (Z' $> 10^9 \Omega\cdot\text{cm}^2$). However, the arc radius first increased and then decreased with increasing WCR content. The N-HAR-1.5/WCR-15 coating showed the largest arc radius ($\sim 6.02 \times 10^9 \Omega\cdot\text{cm}^2$), indicating the most compact and defect-free microstructure. For coatings with WCR content below 10 wt% (e.g., 5 wt%), the smaller arc radius is attributed to insufficient hydrophobic segments to fully densify the matrix. Conversely, for coatings with WCR content above 20 wt% (e.g., 35 and 50 wt%), the reduced arc radius suggests that excessive WCR loading led to local aggregation and phase separation, disrupting the integrity of the crosslinked network and introducing micro-defects that serve as potential pathways for electrolyte ingress. After 60 days of immersion, the N-HAR-1.5/WCR-15 coating retained the largest arc radius ($Z' \approx 5.8 \times 10^9 \Omega\cdot\text{cm}^2$), demonstrating the durability of its physical barrier structure. In contrast, coatings with WCR > 20 wt% exhibited significantly contracted arcs (e.g., N-HAR-1.5/WCR-50: $Z' \sim 1.5 \times 10^9 \Omega\cdot\text{cm}^2$), confirming that excessive WCR compromises long-term barrier stability by the strong van der Waals interactions between the chlorine atoms in their polymer chains.

b. Bode magnitude plot variation

The low-frequency impedance modulus ($|Z|_{0.01}$ Hz) correlates positively with WCR content up to 15 wt%: N-HAR-1.5/WCR-15 maintains $|Z|_{0.01}$ Hz $> 10^{10} \Omega\cdot\text{cm}^2$ after 60 days, which is one order of magnitude higher than N-HAR-1.5 (without WCR, $|Z|_{0.01}$ Hz $\sim 3.71 \times 10^5 \Omega\cdot\text{cm}^2$) and N-HAR-1.5/WCR-50 ($|Z|_{0.01}$ Hz $\sim 8.2 \times 10^8 \Omega\cdot\text{cm}^2$). Beyond 15 wt% WCR, $|Z|_{0.01}$ Hz decreases gradually because excessive WCR dilutes crosslinking sites and causes phase separation, weakening the barrier effect.

c. Bode phase angle characteristics

The phase angle plateau width (near -90°) reaches a maximum at 15 wt% WCR (frequency range: 10^2 – 10^4 Hz), indicating the densest coating structure with minimal defects. For WCR < 10 wt%, the plateau is narrower due to insufficient hydrophobicity; for WCR > 20 wt%, the plateau shrinks and phase angle drops to -65° – -50° after 60 days, as WCR agglomeration creates ion diffusion channels. Only N-HAR-1.5/WCR-15 retains a broad plateau (-85° – -90°) after long-term immersion, confirming its superior capacitive behavior and barrier stability.

These results collectively confirm that 15 wt% WCR achieves optimal synergy with the 1.5 wt% NMA/HEA crosslinking network: moderate WCR content enhances hydrophobicity and densifies the microstructure, while excessive WCR undermines structural integrity by disrupting network continuity and inducing phase separation due to the strong van der Waals interactions between the chlorine atoms in their polymer chains. This finding aligns with the conclusion that precise WCR dosage is critical for balancing barrier performance and long-term corrosion resistance.

To gain deeper insight into the corrosion protection mechanism of the composite coating system [40,41], this study analyzed the evolution of coating resistance (R_c) and charge transfer resistance (R_{ct}) during long-term immersion through equivalent circuit fitting (detailed in Supporting Information Fig. S2). Analysis of key electrochemical parameters indicates that the N-HAR-1.5/WCR-15 coating exhibits exceptional barrier durability: its R_{ct} value remained stably high at approximately $10^{10} \Omega\cdot\text{cm}^2$ after 60 days of immersion, significantly surpassing those of the N-HAR-1.5 ($\sim 10^5 \Omega\cdot\text{cm}^2$) and N-HAR-0 ($\sim 10^3 \Omega\cdot\text{cm}^2$) coatings. This sustained high R_{ct} , which is several orders of magnitude above the other formulations, directly confirms that the coating maintained its structural integrity throughout the immersion period, effectively preventing electrolyte penetration and thereby inhibiting the initiation of interfacial electrochemical corrosion reactions. The consistently high R_{ct} value is not a consequence of any

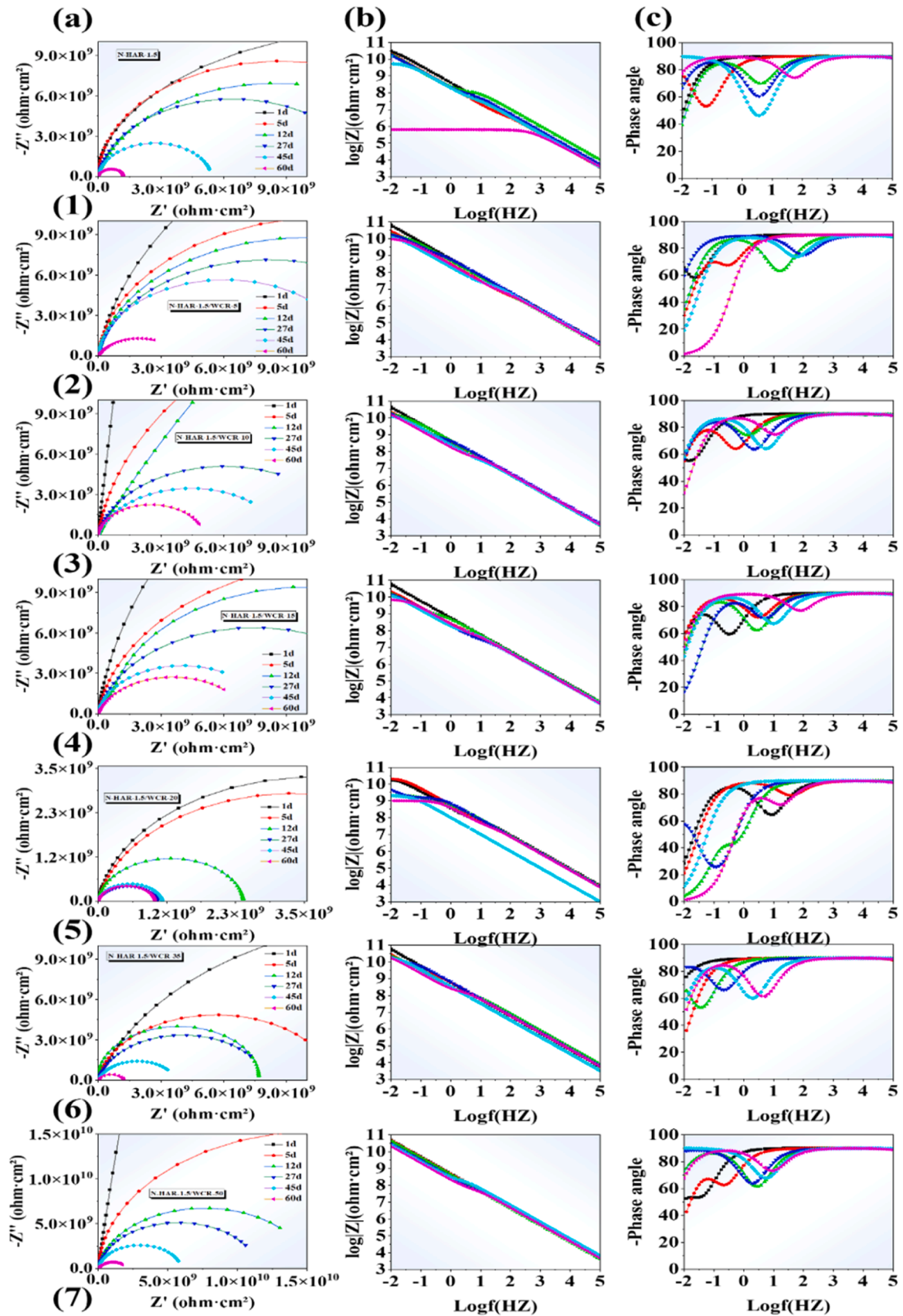


Fig. 10. Evolution of electrochemical impedance behavior for N-HAR-X/WCR-Y composite coatings during prolonged corrosion exposure. (a) Nyquist. (b) Bode magnitude. (c) Bode phase angle representations. (1) N-HAR-1.5; (2) N-HAR-1.5/WCR-5; (3) N-HAR-1.5/WCR-10; (4) N-HAR-1.5/WCR-15; (5) N-HAR-1.5/WCR-20; (6) N-HAR-1.5/WCR-35; (7) N-HAR-1.5/WCR-50.

chemical inhibition layer formed at the interface, but rather a direct reflection of the coating's superior physical barrier performance: with no corrosive species reaching the metal substrate, no corrosion reactions can occur. This "dual physical barrier" synergistic mechanism—combining the dense crosslinked network from NMA/HEA and the strong van der Waals interactions between the chlorine atoms from well-dispersed WCR—is the fundamental reason for the exceptional long-term corrosion resistance exhibited by the N-HAR-1.5/WCR-15 composite coating.

4. Conclusion

This study achieves a critical innovation in waterborne organic anticorrosive coatings by integrating NMA/HEA covalent crosslinking with waterborne chlorinated rubber (WCR) interfacial functionalization, breaking the traditional limitation of simple physical blending between acrylic resins and chlorinated rubber and proposing a novel "dual physical barrier" protection mechanism—the core theoretical innovation of this work. The NMA/HEA crosslinking network densifies the coating structure to form a robust primary physical barrier against corrosive medium penetration, while WCR synergistically enhances the coating's hydrophobicity and promotes the formation of an ultra-compact secondary physical barrier, collectively constructing a highly tortuous diffusion path that effectively block the transport of water, oxygen, and chloride ions to the metal interface. This dual physical barrier mechanism fundamentally addresses the inherent defects of pure waterborne acrylic coatings, including poor water resistance, insufficient wet adhesion, and limited long-term corrosion resistance. The study further clarifies the synergistic regulation law of crosslinking density and WCR content on coating performance, providing a precise formulation design strategy for the composite modification of waterborne anticorrosive coatings. This dual physical barrier mechanism enriches the theoretical system of barrier-type organic coatings for corrosion protection, providing a precise formulation design strategy for the composite modification of waterborne anticorrosive coatings. The prepared eco-friendly composite coating, with its balanced mechanical properties and outstanding long-term corrosion resistance, offers a feasible technical pathway for the green upgrading of anticorrosive coatings intended for harsh chloride-containing environments. While this work advances the field, challenges remain, particularly the limited thermal stability of the WCR-containing system. As evidenced by TGA (Fig. 6d), WCR undergoes initial thermal degradation commencing around 150–200 °C via a dehydrochlorination process, releasing hydrogen chloride (HCl). This not only results in mass loss and the potential formation of micro-voids within the coating matrix, but may also catalyze further degradation of the acrylic network at elevated temperatures, thereby compromising the long-term structural integrity of the coating under high-temperature service conditions. Future research should therefore focus on WCR modification strategies to enhance its thermal resistance (e.g., stabilization against dehydrochlorination), in-situ characterization of barrier layer evolution under thermal stress, molecular-level design of more thermally robust composite systems, and the development of scalable preparation processes to facilitate industrial application. The dual physical barrier mechanism also provides a new research perspective for the design of high-performance waterborne organic coatings tailored for diverse harsh service scenarios.

CRedit authorship contribution statement

Haohan Huang: Conceptualization, Methodology, Validation, Investigation, Data curation, Writing – original draft, Visualization. **Yong Zhang:** Methodology, Investigation, Data curation, Writing – review & editing. **Congcong Zhang:** Investigation, Data curation. **Rulin Li:** Data curation, Formal analysis. **Qiang Lei:** Resources, Investigation. **Dongpeng Wang:** Formal analysis, Visualization. **Zhengbai Zhao:** Resources, Investigation. **Zhaolei Li:** Methodology, Supervision. **Lizhuang**

Chen: Validation, Writing – review & editing. **Weili Li:** Conceptualization, Resources, Supervision, Funding acquisition, Writing – review & editing, Project administration.

Declaration of competing interest

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

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.surfin.2026.109930](https://doi.org/10.1016/j.surfin.2026.109930).

Data availability

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

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