

Investigate the performance of functional coatings with physically modified boron nitride composite fillers

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ARTICLE INFO

Keywords:

Hexagonal boron nitride
Physical encapsulation
Thermal conductivity
Metal corrosion protection
Mechanical property

ABSTRACT

Fillers play a pivotal role in endowing coatings with multifunctional properties. Hexagonal boron nitride (h-BN), a lamellar nanofiller, can significantly enhance the thermal conductivity, corrosion resistance, and mechanical properties of polymer resin-based coatings due to its unique structural features. However, the significant surface energy mismatch between h-BN (a low-polarity inorganic material) and polar organic polymers leads to poor interfacial wettability and phase separation tendencies. Simultaneously, the high specific surface area of BN nano/micro particles promotes agglomeration driven by hydrogen bonding, π - π stacking, or electrostatic forces (e.g., charged surfaces). This study employs an environmentally friendly physical encapsulation strategy to modify h-BN using silica sol, while leveraging the porous structure of dried silica sol to adsorb the corrosion inhibitor benzotriazole (BTA), thereby synergistically improving the corrosion resistance of the coating. FE-SEM observations confirm that silica sol successfully constructs a porous morphology on the surface of lamellar BN, effectively inhibiting filler agglomeration in the resin. The introduction of modified BN increases the coating hardness to 3H, with in-plane and through-thickness thermal conductivities improving by 1332 % and 342 %, respectively, compared to pure epoxy coatings. Electrochemical impedance spectroscopy (EIS) and salt spray tests demonstrate a remarkable enhancement in corrosion resistance. This research provides a novel approach for the application of h-BN in functional protective coatings.

1. Introduction

Metals are recognized as indispensable components in modern society, due to their excellent physical and chemical properties. They have been widely used across various fields. Corrosion, a phenomenon that damages metals, is a significant issue [1]. Except for a few precious metals, most metals are susceptible to instantaneous corrosion in our daily environment, leading to substantial economic losses and environmental pollution. Over the past few decades, countless incidents of oil spills, explosions, and environmental pollution have been caused by corrosion of metals. Therefore, the development of technologies for metal protection is of utmost importance [2]. Numerous methods are known to prevent metal corrosion, including the use of corrosion-

resistant alloys, electrochemical protection, electroplating, and polymer coatings. Among these, organic coating has gained popularity due to its effective protection, ease of preparation, and low cost [3,4].

In organic coatings, polymer resins are the primary and fundamental components, also known as binders. They serve to bind pigments and fillers together and form a uniform and dense film on the substrate [5], and thus, determine the properties of the film, such as paint. However, polymer resins alone cannot provide various special properties of a coating. To overcome this problem, inorganic nanosheets with different characteristics, such as anti-corrosion, thermal conductivity, electrical conductivity, and reinforcement properties, are used to functionalize polymer coatings. Those inorganic nanosheets include hexagonal boron nitride (h-BN), graphene, nano-zinc oxide (ZnO₂), montmorillonite clay,

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TiO₂, CaCO₃, SiO₂, Al₂O₃, Ag, and carbon nanotubes, and so on [6,7]. However, inorganic nanosheets have a high specific surface area, which leads to strong van der Waals forces and other intermolecular forces, causing nanoparticles to aggregate into clusters in the coatings to reduce the overall surface energy of the system.

To overcome this deficiency, modifying the surface of nanosheets has become a reliable solution. On one hand, it enables effective dispersion of nanosheets in resins; on the other hand, it bestows new properties upon the modified nanosheets. Yiting Xu et al. proposed a method to modify the hexagonal boron nitride with maleimide functional groups, which was then doped into epoxy coating [8–10]. The cured composite coating showed an excellent anti-corrosive property based on the Diels-Alder reaction. Ehsan Javadi et al. modified nano-ZnO₂ with 3-(2-aminoethyl amino) propyl trimethoxy-silane and applied it to acrylic-based coatings. EIS results showed that the added silane-modified nano-ZnO₂ increased the protection performance of coatings [11].

h-BN is a layered nanosheets, covalently bonded by nitrogen and boron, forming a two-dimensional sheet of atoms held together by weak van der Waals forces. This material possesses high mechanical strength, flexibility, good thermal conductivity, and excellent chemical stability [12]. Additionally, because the coating doped with h-BN exhibits high electrical insulation performance, it does not require the formation of a galvanic cell with the underlying metal, thereby providing effective anti-corrosion protection.

Regrettably, the utilization of h-BN within the area of polymer nanocomposites is significantly constrained by its inadequate dispersion characteristics. Traditionally, the standard approach for the functionalization of h-BN encompasses a process of etching, predominantly executed via hydroxylation utilizing concentrated acidic or alkaline solutions. This treatment facilitates the introduction of hydroxyl functional groups onto the surface of h-BN (OH-BN), which can interact with the polymer matrix and successfully transfer the load between h-BN and the polymer, forming a very effective material for strengthening the polymer matrix [13]. However, this method poses environmental hazards, and the strong acid can oxidize the edges of h-BN.

Based on the research findings from our previous work, the physical encapsulation method was applied to coat the surface of h-BN with silica sol and then cure it through baking to form a composite nanosheets [14,15]. Firstly, a sol-gel technique was applied to directly grow mesoporous silica on the surface of h-BN nanosheets. Then, BTA, the corrosion inhibitor was introduced into the h-BN decorated mesoporous silica to create a multidimensional BTA-SiO₂@h-BN filler, which was later added to epoxy to obtain the modified advanced composite coating [16]. The resulting composite coating, with optimized loading, demonstrated superior corrosion protection, thermal conductivity, and mechanical properties, making it suitable for all these various applications [17]. Subsequently, a corrosion inhibitor, BTA is adsorbed onto its surface to endow the composite nanosheets with anti-corrosion properties. At last, the modified composite nanosheets was incorporated into epoxy resin to fabricate an epoxy-based composite coating. The mechanical properties, thermal conductivity, and corrosion resistance of the resulting coating were meticulously evaluated, with particular attention given to the characteristics imparted by the composite filler.

2. Experimental section

2.1. Raw materials/regents

Stacked hexagonal boron nitride (h-BN), characterized by its layered structure and large size distribution of 10–15 μm, was provided by Shanghai Mclin Biochemical Technology Co., Ltd. Water-dispersible silica sol (MSE-2, 20%wt) was purchased from Zhejiang Yuda Chemical Co., Ltd. Their morphologies were observed using FESEM, which are presented in Fig.S1(a), (b) [18], respectively. Benzotriazole (BTA) was bought from Guangzhou Fufei Chemical Technology Co., Ltd. Epoxy resin (epoxy value: 0.51 mol/100 g) was acquired from Nantong Star

Synthetic Materials 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. Wet-ting dispersant (YCK-2601), leveling agent (YCK-1110), and defoaming agent (YCK-810) were generously supplied by Shanghai ICKE Chemical Technology Co., Ltd.

2.2. Encapsulation of the h-BN nanosheets with silica sol

Initially, deionized water and propylene glycol methyl ether (PM) were mixed with a volume ratio of 1:1 to form a mixed solvent. Subsequently, YCK-2601 was introduced as a wetting dispersant. Following this, the h-BN nanosheets and water-dispersible silica sol were added in equal mass ratios. The mixture underwent ultrasonic dispersion for 1 h to ensure homogeneity. Afterward, the mixture was stirred for an additional hour using grinding balls at a rotation speed of 1000 rpm to further enhance dispersion. Ultimately, the mixture was processed using a rotary evaporator to remove the solvent, yielding paste-like powders. Raw materials for preparing SiO₂@h-BN composite nanosheets and their proportion are present in Table S1. Afterwards, the corrosion inhibitor BTA was dissolved in the butyl acetate at a concentration of 5%wt and loaded onto the composite nanosheets via solution immersion to obtain the BTA-SiO₂@h-BN, which was later used as fillers to enhance the properties of epoxy-based coatings. The preparation process is depicted in Fig. 1(a).

2.3. Preparation of the composite coatings doped with BTA-SiO₂@h-BN

To fabricate composite coatings doped with BTA-SiO₂@h-BN an aqueous epoxy dispersion (AEP-Dispersion) was first prepared. A blended mixture of epoxy resin and epoxy emulsifier was prepared at a weight ratio of 10:1. After thorough mixing, the blended mixture was heated to 80 °C, to which deionized water was added gradually. The mixture was stirred at a high speed of 800 rpm using a high-speed disperser during the dropwise addition of deionized water. After the water addition was completed, the mixture was further stirred at a high speed for 1 h at 80 °C. The solid content of the AEP-Dispersion was maintained at 60%wt.

Subsequently, the AEP-Dispersion served as the polymer matrix, and the previously prepared BTA-SiO₂@h-BN was incorporated as the functional nanosheets into the system. The mixture was stirred at a rate of 1500 rpm for 2 h at room temperature to ensure even dispersion. The relative content of BTA-SiO₂@h-BN to the epoxy resin was adjusted to 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt%, to evaluate the impact of the relative content on the performance of the cured coatings; and the detailed formula are listed in Table S2 ~ S6. For the ease of description, the prepared composite coatings were designated as BTA-SiO₂@h-BN-EP-X, where X represents the weight percentage of BTA-SiO₂@h-BN (i.e., X = 5, 10, 15, 20, 25, respectively).

To examine the cross-sectional morphology of the coatings derived from BTA-SiO₂@h-BN-EP-X, and explore the correlation between morphology and the properties of the cured coatings, steel panels and silica glasses were utilized as substrates and coated with BTA-SiO₂@h-BN-EP-X at room temperature. Before coating, the steel panels were polished with sandpaper and subsequently cleaned with alcohol to remove dust. During the curing process, a series of BTA-SiO₂@h-BN-EP-X, along with coalescing curing agents and flash rust inhibitors, were thoroughly mixed and applied to the prepared substrates using a winding bar. The coatings were allowed to dry at room temperature for 7 days (168 h), with the thickness of the coatings being controlled at 90 μm and 60 μm. The schematic representation of the preparation of BTA-SiO₂@h-BN and BTA-SiO₂@h-BN-EP-X is depicted in Fig. 1(b).

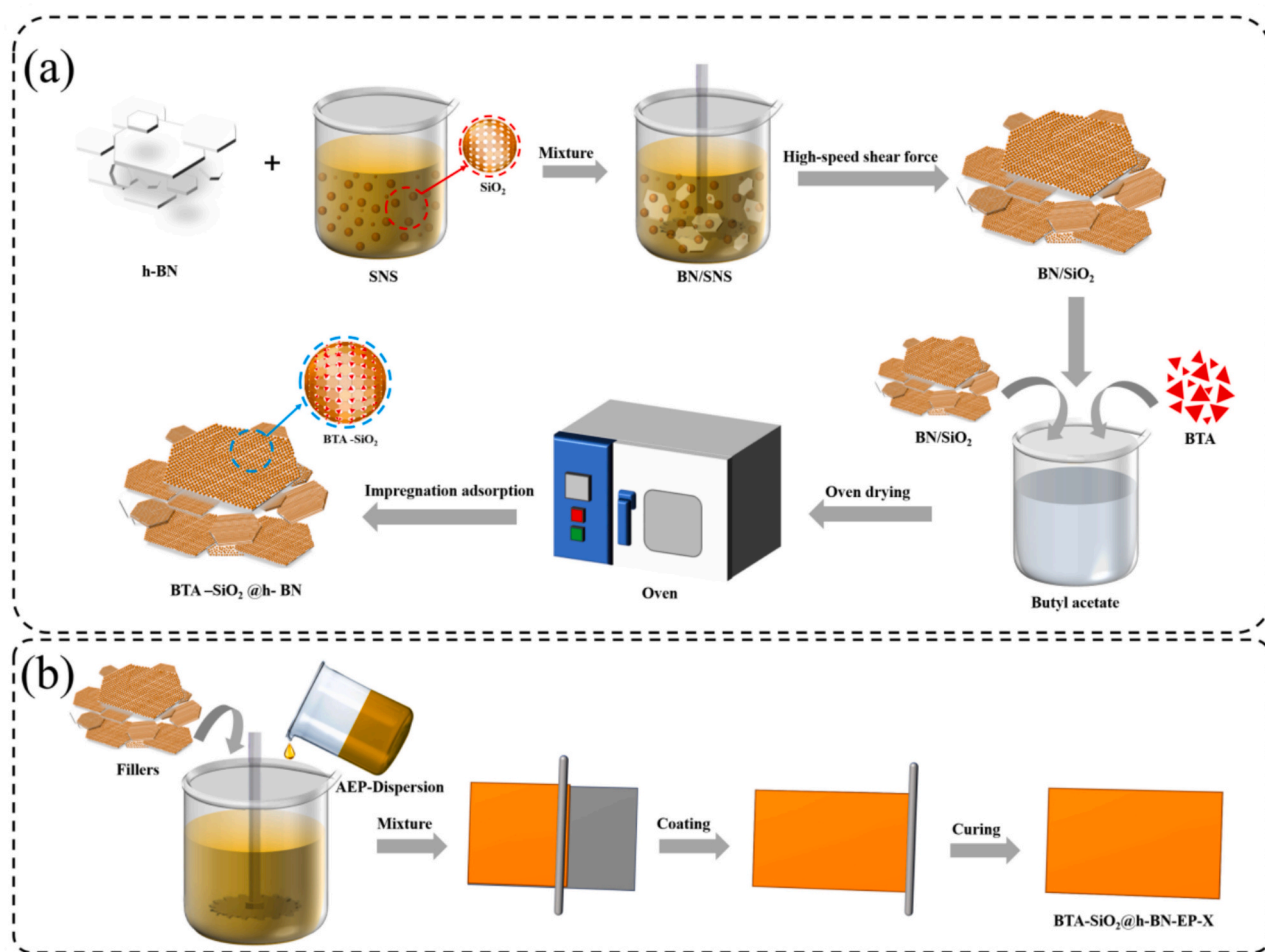


Fig. 1. Schematic Diagram of the Preparation Process for (a) BTA-SiO₂@h-BN; (b) BTA-SiO₂@h-BN-EP-X coating.

2.4. Characterization of materials

Fourier transform infrared (FTIR) spectroscopy was conducted using a Nicolet iS 50 FTIR spectrometer (Thermo Fisher Technologies, USA). The cross-sectional morphology of the cured coatings was characterized by a Zeiss Merlin Compact field emission scanning electron microscope (Carl Zeiss, Germany). The phase and crystal structure analysis of h-BN and BTA-SiO₂@h-BN were performed using X-ray diffraction (XRD) on an XRD-6000 X-ray diffractometer (Shimadzu Corporation, Japan). The XRD measurements were carried out at a voltage of 40 keV with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a 2θ range from 10° to 90° .

The thermodynamic properties of the cured composite coatings were characterized via NETZSCH DSC214 (NETZSCH, Germany). The thermal stability of the coatings was analyzed by a Diamond TG-DTA thermogravimetric analyzer Perkin Elmer Instruments.

The mechanical properties of the coating were evaluated through a series of standardized tests. Hardness was ascertained by using Trolley pencil hardness tester BGD 506/1 according to the GB/T 6739–2006 method. Flexibility was assessed with a QTX-type paint film elasticity tester, manufactured by Tianjin Jinghai Kexin Test Machine Factory, in accordance with GB/T1731–2020. Impact resistance was determined utilizing the BGD302 tubular film impactor, adhering to the guidelines of GB/T 20624.2–2006. Tensile adhesion was quantified with a BGD500 coating digital display testing machine, following the protocol of GB/T 5210–2006. The friction resistance of the coatings were evaluated using the BGD 523 paint film wear tester according to GB/T 1768–2006. Product of Biuged Precision Instrument (Guangzhou) Co., LTD. All testing equipment was provided by Biuged Instruments Co., Ltd.

The thermal conductivity of the samples was determined using the LFA-467 Nano-flash thermal conductivity tester, which was sourced from Neotsu Scientific Instrument Trading (Shanghai) Co., LTD. Concurrently, thermal conductivity observations were facilitated by the HIKMICRO H36 infrared thermal imaging instrument. The temperature-dependent response of the samples was profiled from 20 to 60 °C.

The corrosion resistance of the coating was evaluated using the analysis of the AC impedance spectrum and the Tafel polarization curve. The electrochemical characterization was performed using a CS2350H electrochemical workstation, provided by Wuhan Coster Instrument Co., LTD. A 3.5 wt% NaCl solution was employed as the corrosive medium. The electrochemical cell configuration comprised a platinum electrode as the counter electrode (CE), a saturated calomel electrode as the reference electrode (RE), and the coated iron plate served as the working electrode. The exposed area of the coating was approximately 9.6 cm². The Tafel polarization curve was generated at a scanning rate of 2.5 mV/s over a potential range of $\pm 0.25 \text{ V}$ relative to the open circuit potential. Following this, AC impedance measurements were conducted across a frequency range from 100 kHz to 0.01 Hz, with an AC amplitude of 10 mV perturbation applied relative to the open circuit potential.

Following the electrochemical assessments, a salt spray test was conducted using a YWX/Q-250 salt spray test chamber to further investigate and analyze the coating's corrosion resistance.

3. Results and discussion

3.1. Analyzing the morphologies and properties of BTA-SiO₂@h-BN nanosheets

To investigate the influence of silica-sol on the morphological and physicochemical properties of h-BN nanosheets, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD) analyses were employed.

Fig. 2(a) depicts the Fourier-transform infrared spectroscopy (FTIR) spectra of silica sol, h-BN, and BTA-SiO₂@h-BN, respectively. The spectral features at 471 cm⁻¹ and 1112 cm⁻¹ are indicative of the deformation and symmetric stretching vibrations of the Si-O-Si bond, respectively [19]. The peak observed at 785 cm⁻¹ is attributed to the antisymmetric stretching vibration of the Si-O-Si bond. Additionally, the peak at 960 cm⁻¹ and the broad band ranging from 3388 cm⁻¹ to 3459 cm⁻¹ are associated with the deformation and stretching vibrations of the Si-OH bond. The presence of a peak at 1637 cm⁻¹ is attributed to the absorption by water molecules [20]. In the case of h-BN, two prominent

characteristic peaks are discernible at 822 cm⁻¹ and 1378 cm⁻¹, corresponding to the in-plane B—N tensile vibration and out-of-plane B-N-B bending vibration, respectively, as referenced in literature. The FTIR spectra confirm the coexistence of the characteristic absorption peaks of both constituents, thereby suggesting that the silica sol and h-BN have been effectively compounded.

Fig. 2(b) depicts the results of X-ray diffraction (XRD) analysis. Both of the two samples exhibit distinct BN(002) and (004) peaks at 26.7° and 55.0°, respectively. The BTA-SiO₂@h-BN nanosheets maintain the typical peak shapes associated with the layered structure of h-BN. The sharpness of the peaks and the intact structure confirm that the physical hybridization with silica sol did not compromise the intrinsic structure of h-BN [21]. However, for the BTA-SiO₂@h-BN nanosheets, the encapsulation by amorphous silica sol affects the intensity of the main peak at (002), indicating successful encapsulation of silica sol on h-BN. Due to the low adsorption amount of BTA on the surface of the composite nanosheet, its characteristic peaks are obscured by other chemical substances in the FTIR and XRD spectra [22].

Fig. 2(c) presents the FESEM images of the BTA-SiO₂@h-BN

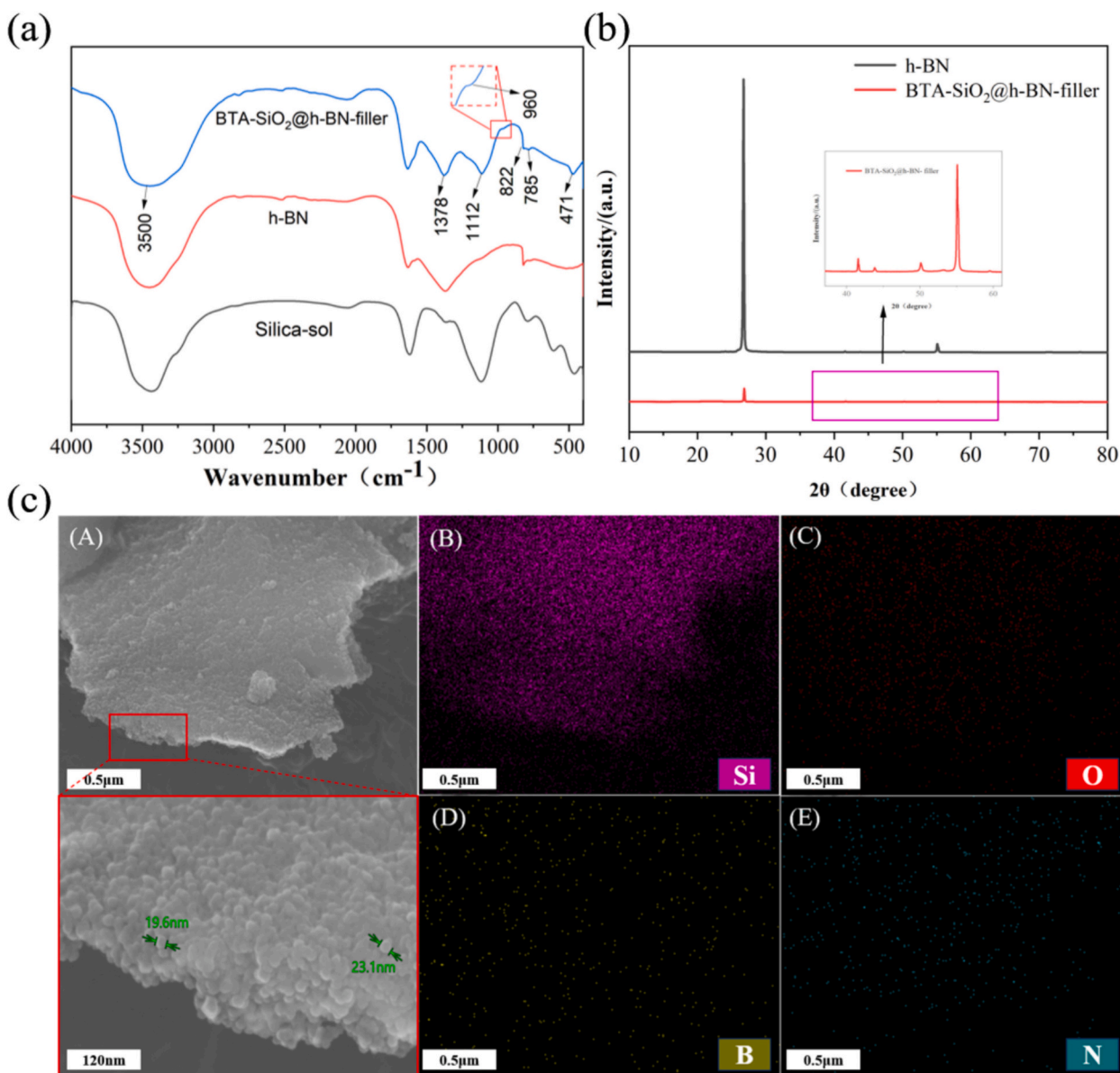


Fig. 2. (a) FTIR spectra and (b) XRD analysis of the BTA-SiO₂@h-BN nanosheets and the corresponding raw material; (c) FESEM images of BTA-SiO₂@h-BN and the corresponding EDS spectra of elements.

nanosheets, revealing a distinct morphology compared to that of pristine h-BN. The h-BN nanosheets are effectively encapsulated and integrated with amorphous SiO_2 upon drying, a process that is attributed to the surface modification techniques employed. Then, BTA can be easily adsorbed into the porous morphology of SiO_2 on the surface of h-BN. In addition, this encapsulation and integration are hypothesized to mitigate the aggregation phenomena when the BTA- SiO_2 @h-BN nanosheets are introduced into a polymer matrix. As depicted in Fig. 2(c)-(B) to (F), EDS was utilized to analyze the elemental distribution of Si, O, B, and N on the surface of BTA- SiO_2 @h-BN nanosheets. The uniform distribution of these elements across the composite is indicative of a homogeneous dispersion, which is a critical factor in ensuring the performance of the coatings when they are doped into the polymer matrix [23]. These findings substantiate the successful fabrication of the BTA- SiO_2 @h-BN nanosheets.

3.2. The interference of BTA- SiO_2 @h-BN nanosheets on the morphologies of the composite coatings

The distribution of nanosheets within a coating is a critical determinant of its performance characteristics. This section investigates the effects of various concentrations of BTA- SiO_2 @h-BN nanosheets, from 0%wt to 25%wt, on the cross-sectional morphologies of the composite coatings, as depicted in Fig. 3. It was observed that an elevation in the concentration of these doped nanosheets leads to the filling of voids within the cured resins [24]. Furthermore, the presence of colloidal silica-sol on the surface of h-BN particles and the ensuing irregular morphologies facilitate the effective occupation of interstitial spaces between boron nitride during the curing process. This phenomenon is instrumental in preventing the aggregation of nanosheets, thereby ensuring their homogeneous dispersion within the polymer matrix [25]. As the content of BTA- SiO_2 @h-BN in the coating increases, the nanosheets gradually form interconnections, establishing a three-dimensional thermal conduction network through thermal channels that interlink the filler particles. Concurrently, the characteristic “maze” effect, which is ascribed to the physical barrier properties of the two-dimensional morphology fillers, elongates the path for corrosive media to penetrate the coating [26]. This extension of the infiltration

pathway enhances the corrosion resistance of the cured coatings.

3.3. The enhancement of thermodynamic properties of the composite coating by the BTA- SiO_2 @h-BN nanosheets

(i) TGA measurement

The TGA curves depicted in Fig. 4 illustrate the thermal degradation profiles of a series of specimens, encompassing a AEP-Dispersion based coating, a BN-EP-25, and a BTA- SiO_2 @h-BN-EP-25, thereby elucidating the incorporation of different nanosheets on the thermal properties of the cured coatings [27,28]. In the initial stage, all specimens exhibit a gradual mass reduction from 25 °C to 332 °C, which is attributed to the thermal decomposition of residual organic solvents that were present during the curing process. Above 454 °C, the thermal decomposition of

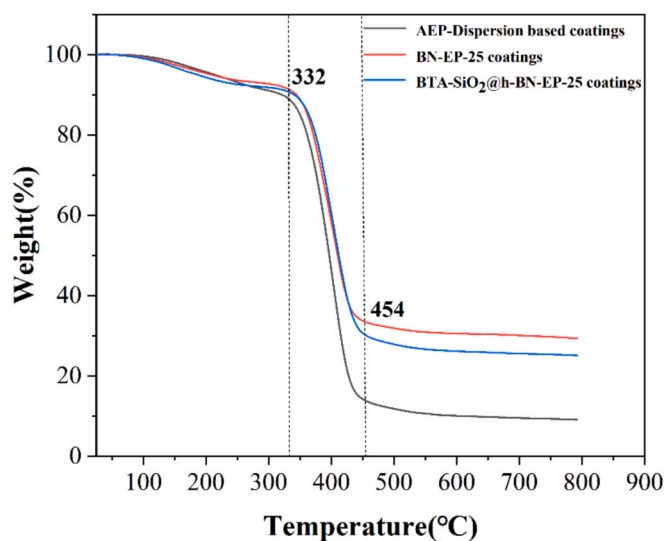


Fig. 4. TGA images of AEP-Dispersion based coating, BN-EP-25, and BTA- SiO_2 @h-BN-EP-25 coatings.

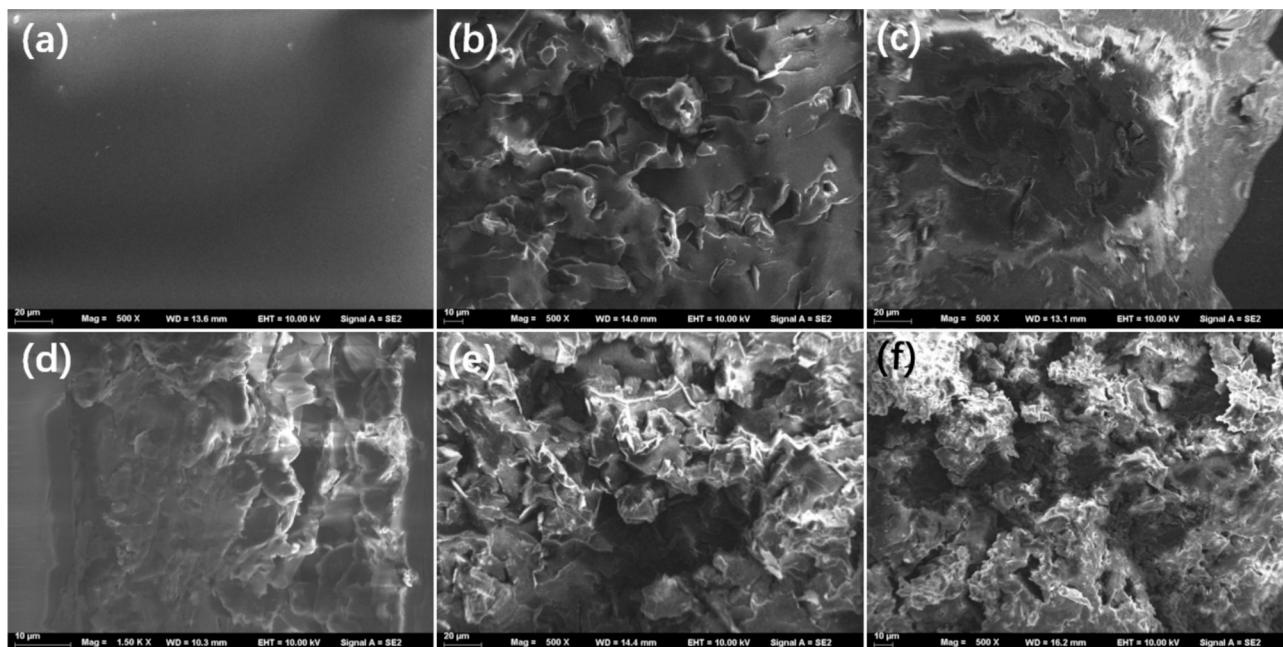


Fig. 3. FESEM images of the cross-section of the cured coatings (a) pure epoxy-based coatings; (b) BTA- SiO_2 @h-BN-EP-5; (c) BTA- SiO_2 @h-BN-EP-10; (d) BTA- SiO_2 @h-BN-EP-15; (e) BTA- SiO_2 @h-BN-EP-20; (f) BTA- SiO_2 @h-BN-EP-25.

the test specimens is deemed to be completed. The pristine epoxy-based coating experiences progressive thermal decomposition, culminating in a weight loss of approximately 90 % (w/w), with only residual carbonaceous material remaining, as referenced in literature [29]. In contrast, the h-BN-EP-25 coating remains undecomposed, because of the exceptional high-temperature stability of hexagonal boron nitride (h-BN) can endure temperatures up to 3000 °C. As a result, its composite coating manifests the highest residual mass post-pyrolysis. Regarding the BTA-SiO₂@h-BN-EP-25 coating, the silica sol on the surface of h-BN undergoes continuous dehydration and condensation reactions within the experimental temperature range, resulting in a more significant weight loss compared to the coating doped solely with h-BN [30]. Upon reaching a critical temperature of 454 °C, the silica sol is fully dehydrated, transforming into silica powder, and no further thermal mass loss is observed. The TGA findings suggest that the silica sol on the surface of h-BN in the composite coating contains silanol groups capable of forming hydrogen bonds [31]. This not only enhances the mechanical properties of the coating but also, in conjunction with the layered structure of boron nitride, impedes the permeation of corrosive media.

(ii) DSC

To further investigate the impact of doped BTA-SiO₂@h-BN on the thermal motion within composite coatings, composite nanosheets with various doping ratios on the T_g of the composite coatings was examined using DSC measurement. Fig. 5 shows that the AEP-Dispersion based coating exhibits a glass transition temperature at 42.4 °C after being cured with polyamide. As the content of the doped BTA-SiO₂@h-BN increases, the T_g of the cured composite coatings gradually rises, reaching a temperature of 69.9 °C from the 25%wt of the doped nanosheets [32]. FESEM images show that a layer of silicic sol is coated on the surface of the h-BN nanosheet, which contains a large number of Si-OH groups. This is beneficial for forming a strong hydrogen bonding interaction between the doped filler and the polymer resin, inhibiting the movement of polymer chain segments, thereby increasing its glass transition temperature. This helps to enhance the hardness of coating and inhibit the permeation of corrosive media through the coating [33,34].

(iii) Heat-conducting property

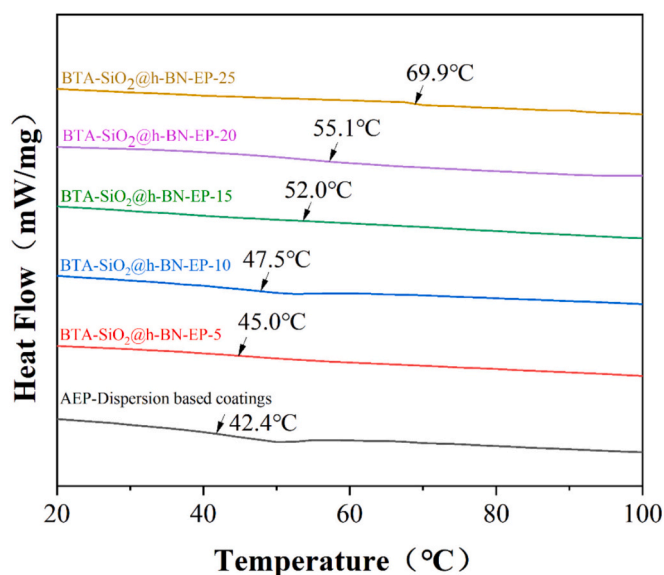


Fig. 5. The DSC curves of BTA-SiO₂@h-BN-EP-X with different content of BTA-SiO₂@h-BN.

The thermal conductivity of composite coatings with various contents of BTA-SiO₂@h-BN was studied to investigate the impact of the doping amount on the thermal conductivity of the cured coatings.

The baseline thermal conductivities of the pure epoxy-based coating are reported as 0.025 W/(mK) for in-plane and 0.18 W/(mK) for through-plane [35]. Upon the incorporation of BTA-SiO₂@h-BN nanosheets, the thermal conductivity of the composite coatings escalates with increasing nanosheets' content [36], as seen in Fig. 6(a). Notably, when the content of BTA-SiO₂@h-BN is 25 wt%, the thermal conductivity of the composite coating in the permeable plane ($K_{\perp}$) achieves 0.358 W/(mK), marking an enhancement of 0.178 W/(mK) over the pure AEP-Dispersion based coating. Meanwhile, the in-surface($K_{\parallel}$) thermal conductivity attains a remarkable 0.795 W/(mK), highlighting a 0.77 W/(mK) improvement over the AEP-Dispersion based coating. Collectively, these findings demonstrate that for the BTA-SiO₂@h-BN-EP-25, its in-plane ($K_{\parallel}$) thermal conductivity is augmented by a factor of 31.8, while the through-plane ($K_{\perp}$) thermal conductivity is elevated by a factor of 2.0 [37]. The coatings doped with composite nanosheets exhibits excellent thermal conductivity. In addition, in the realm of thermal management, the BTA-SiO₂@h-BN-EP-25 coating, as depicted in Fig. 6(b), demonstrates a significant area of color diffusion, indicative of its enhanced in-plane and out-of-plane heat transfer properties relative to other coatings. This remarkable improvement in thermal conductivity is ascribed to the formation of a macroscopic three-dimensional thermal conduction network and a concomitant decrease in thermal resistance at the microscopic interface, the same as elucidated in reference [38].

Fig. 6(c) illustrates that the incorporation of BTA-SiO₂@h-BN nanosheets establishes an extensive phonon transfer pathway between the through-plane and in-plane domains of the composite coating. This pathway facilitates the efficient transfer of phonons within the epoxy resin matrix, thereby augmenting the overall thermal conductivity of the coating.

3.4. The enhancement of the mechanical properties of the composite coatings by BTA-SiO₂@h-BN nanosheets

The mechanical properties of composite coatings were systematically assessed through the evaluation of hardness, flexibility, impact resistance, adhesion, and wear resistance. As delineated in Table 1, an enhancement in the hardness of all the coatings have been observed after incorporating the nanosheets. An increment in the BTA-SiO₂@h-BN content is associated with a progressive enhancement in the hardness, culminating in maximum values of 3H [39]. Conversely, the flexibility of the composite coatings exhibits a decremental trend, with the bending radius increasing from 0.5 mm to 1.5 mm. In comparison with composite coatings doped with pure h-BN, BTA-SiO₂@h-BN nanosheets mitigate filler aggregation within the polymer matrix, facilitating uniform dispersion throughout the cured coatings. Furthermore, with silanol groups on the surface of h-BN, the hydrogen bonding can engage with the resin and metal substrate, thereby enhancing the hardness of the composite coatings. However, the incorporation of rigid BTA-SiO₂@h-BN nanosheets, in conjunction with hydrogen bonding at the filler surface, restricts the mobility of polymer chain segments, leading to a reduction in coating flexibility [40]. Regarding the impact resistance of the composite coatings, the Pigment Volume Concentration (PVC) of the coating remains relatively low within the tested content range, ensuring satisfactory performance. At last, a comparative analysis was conducted between AEP-Dispersion based coatings and composite coatings. The incorporation of h-BN or BTA-SiO₂@h-BN nanosheets were observed to marginally diminish the adhesion between the coatings and the substrate. This reduction in adhesion may be attributed to the fillers' effect on diminishing the interfacial contact between the coating and the substrate.

The study on the impact of added nanosheets on the wear resistance of cured coatings is also very important. Table S7 shows the weight loss of the composite coatings with various BTA-SiO₂@h-BN doping amounts

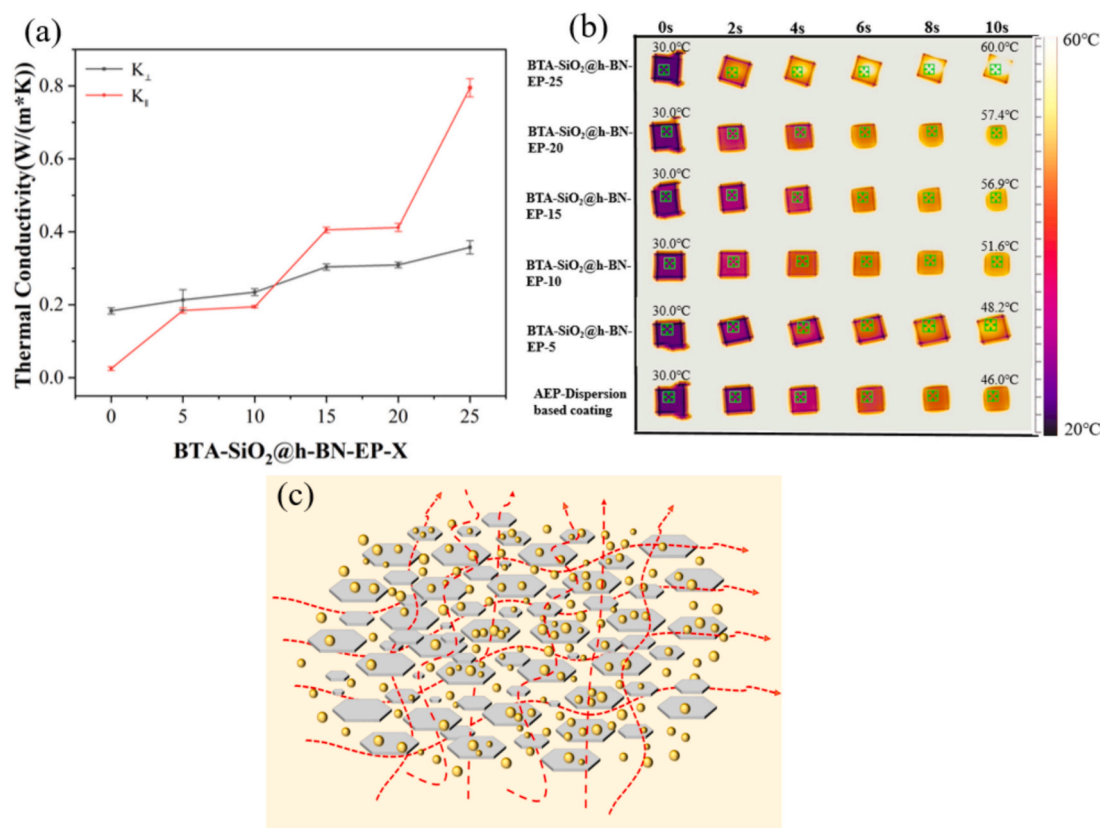


Fig. 6. (a) The thermal conductivity of composite coatings with different contents of BTA-SiO₂@h-BN; (b) The thermal imaging of composite coatings with different contents of BTA-SiO₂@h-BN; (c) The thermal conductivity mechanism of the BTA-SiO₂@h-BN-EP-X coating.

Table 1

Mechanical properties of the composite coatings with various BTA-SiO₂@h-BN content.

Mechanical properties	AEP-Dispersion based coatings	BN/EP-25	BTA-SiO ₂ @h-BN-EP-5	BTA-SiO ₂ @h-BN-EP-10	BTA-SiO ₂ @h-BN-EP-15	BTA-SiO ₂ @h-BN-EP-20	BTA-SiO ₂ @h-BN-EP-25
Hardness	HB	H	H	H	2H	2H	3H
Flexibility(mm)	0.5	1.5	1	1	1.5	1.5	1.5
Impact resistance(kg. cm)	50	50	50	50	50	50	50
Tensile adhesion (Mpa)	2.97	1.98	2.77	2.42	2.23	2.12	2.03

under the abrasion tester from 0 to 450 r. Fig. 7 presents the wear index I calculated from these data according to the Taber ASTM D4060 abrasion standard using Eq. (1). Here, A represents the mass of the sample before abrasion, B represents the mass of the sample after abrasion, C represents the number of abrasion cycles [41], and I represents the coating quality loss rate.

$$I = \frac{(A - B)}{C} \quad (1)$$

As depicted in Fig. 7, the AEP-Dispersion based coating experiences a mass loss of approximately 0.011 g after 450 cycles. Interestingly, when the BTA-SiO₂@h-BN content is elevated to 25 wt%, the mass loss is significantly reduced to 0.003 g, constituting merely 27.3 wt% of the mass loss observed in the pure epoxy-based coating [42]. Fig. 7 clearly illustrates that the initial mass loss rate of the AEP-Dispersion based coating is comparatively elevated and remains superior to that of composite coatings enriched with the BTA-SiO₂@h-BN nanosheets, the same as referenced in literature. In addition, with the incorporation of h-BTA-SiO₂@h-BN, the mass loss rate of the coating exhibits a progressive decline, the coating containing 25 wt% BTA-SiO₂@h-BN demonstrating the most diminutive mass loss rate.

The observed phenomenon can be ascribed to two factors. Firstly, the superior mechanical attributes of h-BN, when uniformly dispersed throughout the polymer matrix, serve as an inorganic filler that augments the hardness of the composite coating, thereby enhancing its resistance to wear. Secondly, the physical modification induced by silica sol facilitates the establishment of hydrogen bonding between the coating and the filler, culminating in the formation of a robust three-dimensional network interlinking the epoxy resin and the boron nitride filler system [43]. This network curtails the slippage of macromolecular chain segments, consequently reducing the frictional loss of the coating, as elucidated in literature. [44]

3.5. The enhancement of the anti-corrosion properties of the composite coatings by the BTA-SiO₂@h-BN nanosheets

In this section, the effect of BTA-SiO₂@h-BN nanosheets on the anti-corrosion properties of the cured coatings was studied. The cured steel plates were immersed in the 3.5 wt% NaCl solution and tested with the Tafel polarization curve and A.C. impedance spectrum.

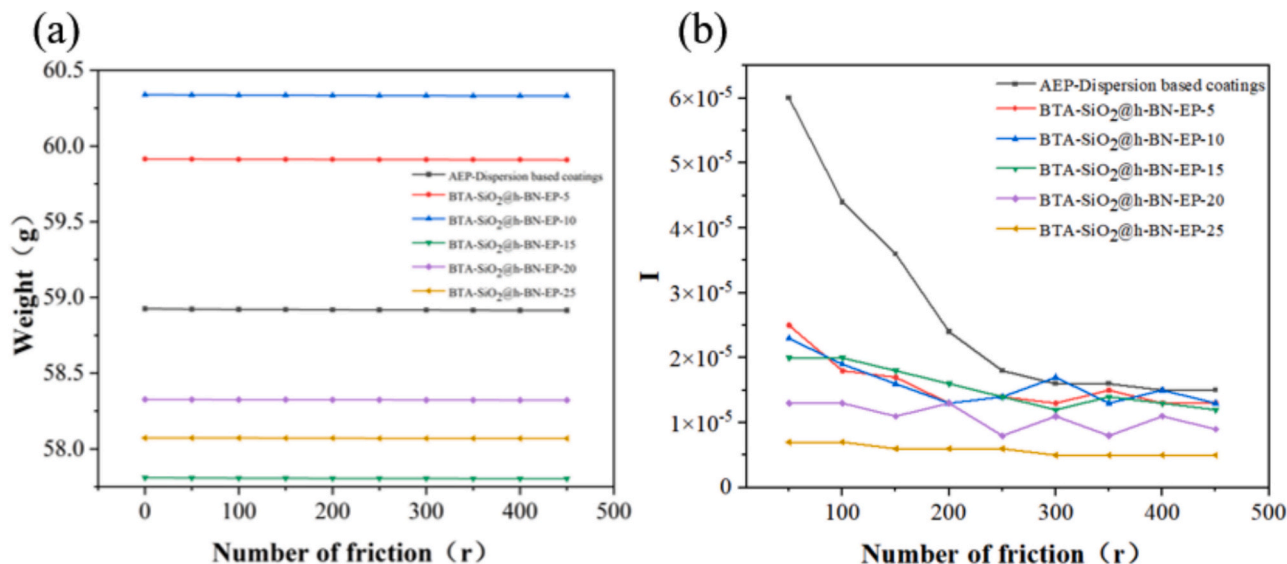


Fig. 7. (a)Coating quality loss; (b)Coating quality loss rate for various composite coatings varied as a function of the number of friction.

3.5.1. Tafel polarization curve

The Tafel polarization curves serve as a diagnostic tool for evaluating the corrosion resistance of coatings by quantifying the variation in corrosion current density (I_{corr}) concerning the applied potential. The corrosion rate (C.R.) can be derived from the Tafel polarization data and is formulated in Eq. (2). This equation establishes a relationship between I_{corr} , C.R., and several constants, as below:

$$C.R. = K \frac{I_{corr} E_w}{\rho} \quad (2)$$

Here, K is the corrosion rate constant (3.27 mm g per (A cm year)), I_{corr} represents the corrosion current density (A cm⁻²), ρ represents the density of carbon steel (7.87 g cm⁻³), and E_w represents the equivalent weight of carbon steel (27.92 g) [45]. Under Faraday's law, the corrosion current density of a coating is directly proportional to its corrosion rate, implying that a reduced I_{corr} corresponds to a decreased corrosion rate for the coating. Additionally, the corrosion potential (E_{corr}) is indicative of the coating's propensity to corrosion; hence, a higher E_{corr} is indicative of superior corrosion resistance. The analysis, of Tafel polarization curves for various coatings, helps to discern and appraise

those exhibiting enhanced anti-corrosion characteristics [46].

Fig. 8 depicts the Tafel polarization curves of the cured coatings with various BTA-SiO₂@h-BN concentrations after a 7-day immersion in a 3.5 wt% NaCl solution. As detailed in Table S8, an increment in the BTA-SiO₂@h-BN content, spanning from 5 wt% to 25 wt%, is associated with a progressive diminution in the self-corrosion current of the composite coating, concomitant with a reduction in the corrosion rate from 1.616×10^{-5} mm/year to 1.50×10^{-7} mm/year. In contrast to the pure EP-based coating, which exhibits a corrosion rate of 7.063×10^{-6} mm/year., the composite coating demonstrates significantly improved corrosion resistance. Optimal corrosion resistance is observed when the BTA-SiO₂@h-BN content is maximized at 25 wt%. This enhancement is likely ascribed to [47] (1) the intrinsic physical barrier attributes and the effective dispersion of the 2D hybrid filler, which engenders a 'maze' effect that impedes the ingress of corrosive media and suppresses cathodic and anodic reactions; and (2) the corrosion inhibitors adsorbed on the surface of the composite nanosheets can chelate with metal ions from the corrosion products, thereby inhibiting further corrosion.

EIS measurements. Here, Carbon steel plates coated with different BTA-SiO₂@h-BN-EP-X coatings were immersed in 3.5 wt% NaCl solution and tested via EIS measurement to investigate the corrosion processes. Generally, the larger the semicircle diameter of the Nyquist diagram, the stronger the corrosion resistance of the coating. The fitted EIS data from the EIS can effectively explain the cause for the failure process of the coating [48]. In the Bode impedance diagram, the low-frequency impedance modulus ($|Z| = 0.01$ Hz) can be an important index to evaluate the anticorrosion ability of a coating, the higher the low-frequency impedance modulus ($|Z| = 0.01$ Hz), the better the anticorrosion ability. In the Bode phase angle diagram, the higher the high-frequency phase angle (close to -90°), the better the integrity of the coating [49].

Fig. 9(a1-f1) presents the Nyquist diagrams for various coatings following the fitting process. The impedance radius arcs consistently diminish with extended immersion periods, signifying a degradation in the coatings' anti-corrosion properties over time, a ubiquitous phenomenon among many coated substrates. For the AEP-Dispersion based coatings, the emergence of two-time constants at the onset of soaking (Fig. 9(a1)) suggests that the corrosive media infiltrates the coating's interior within a few hours, leading to the leaching of soluble metals from the steel surface into the electrolyte solution [50]. The swift deterioration of the AEP-Dispersion based coating can be ascribed to the coatings made solely of polymer resins are ineffective in suppressing the permeation of corrosive media therewithin. A similar phenomenon is observed in the BTA-SiO₂@h-BN-coating-5 % and BTA-SiO₂@h-BN-

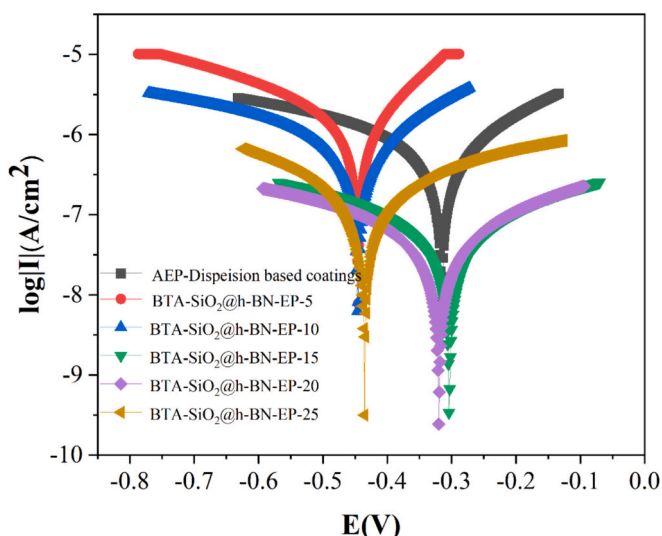


Fig. 8. Polarization curves of the different composite coatings.

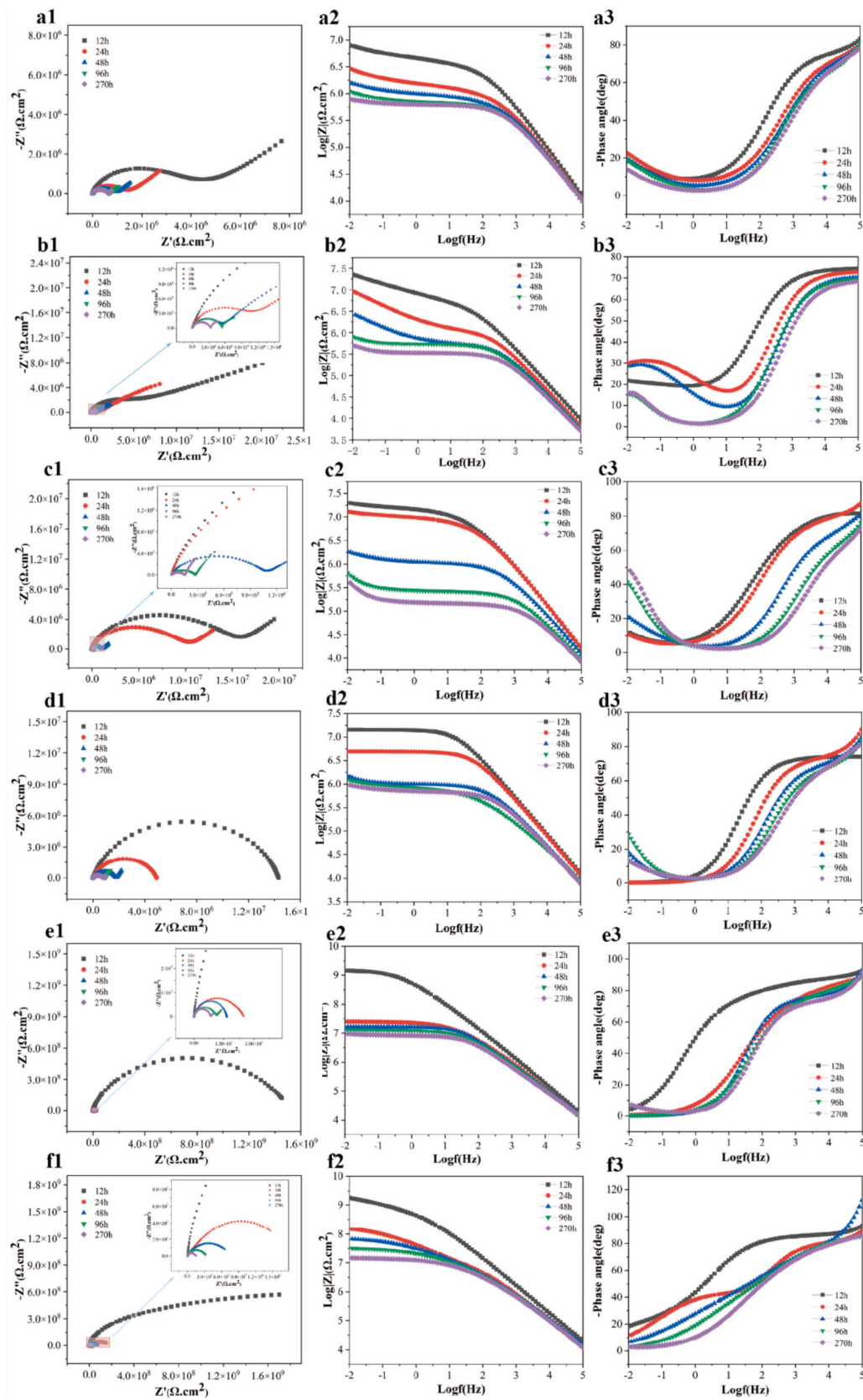


Fig. 9. The EIS diagram of composite coatings with different contents of h-BTA-SiO₂@h-BN. Among them, a is AEP-Dispersion-based coating; and b ~ f are BTA-SiO₂@h-BN-EP-X (X = 5-25%wt), 1-3 are Nyquist diagram, Bode diagram and Phase diagram after fitting, respectively.

coating-10 %, where the impedance arc radius also decreases rapidly with the prolongation of soaking time. This effect is attributed to the insufficient addition of nanosheets, which introduces additional defects and fails to fully exert the cathodic protection effect, culminating in suboptimal coating corrosion resistance [51,52]. However, as the nanosheets content increases, the coating maintains a single time constant during the long-term testing phase, indicating that the coating effectively impedes the penetration of corrosive media onto the metal substrate's surface. In addition, An increased amount of adsorbed BTA can chelate with metal ions generated by corrosion process, thereby more effectively suppressing the continuous progression of corrosion. Notably, the BTA-SiO₂@h-BN-EP-25 coating exhibits the most superior

anti-corrosion performance.

Fig. 9(a2-f2) presents the corresponding Bode diagrams for all the samples, which reflect a similar pattern to the Nyquist diagrams. In general, the low-frequency impedance modulus ($|Z|_f = 0.01$ Hz) is an important indicator for evaluating the corrosion resistance of coatings. The higher the impedance modulus value of a coating, the better its protective and shielding performance [53]. In the early stages of corrosion process (12h), the impedance of the AED dispersion based coating is $8.12 \times 10^6 \Omega \cdot \text{cm}^2$ (Fig 9a2) under in the low-frequency impedance modulus ($|Z|_f = 0.01$ Hz). As the amount of the doped BTA-SiO₂@h-BN increases, the impedance of the composite coating in low-frequency gradually increases. When BTA-SiO₂@h-BN reaches 25 wt%, the

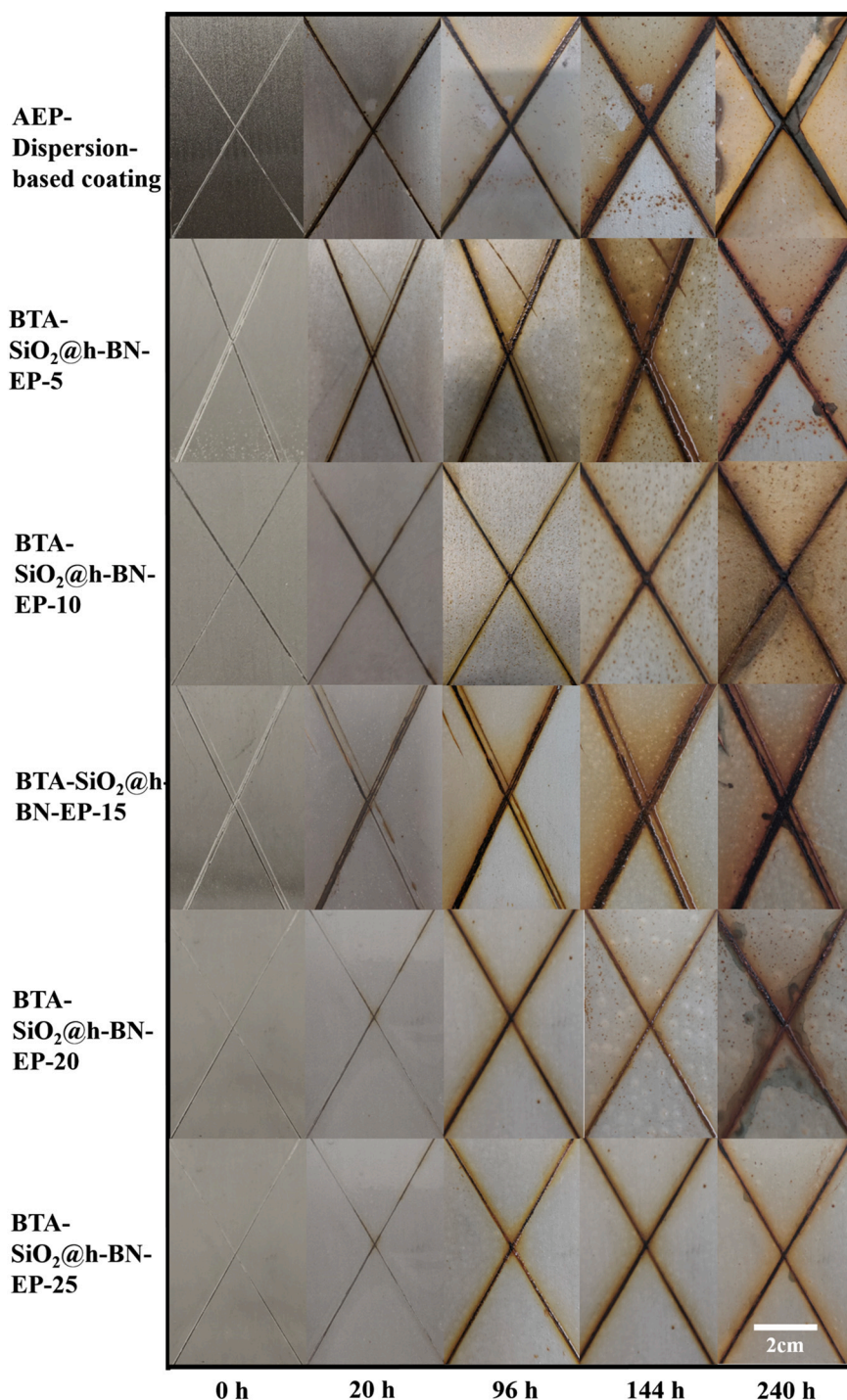


Fig. 10. Digital images of artificial scratch for different coatings after the salt spray test.

impedance of the composite coating reaches $1.80 \times 10^9 \Omega \cdot \text{cm}^2$ (Fig 9f2), which is three orders of magnitude higher than that of AED dispersion based coating. After 270 h of immersion in saline water, the low-frequency impedance modulus of different coatings gradually decreases with the extension of the coating immersion time, indicating that the entry of corrosive media has compromised the coating, leading to a gradual reduction in its corrosion resistance of the coatings [54]. However, the BTA adsorbed in the composite filler can form chelation with the metal ions, and thereby inhibit further corrosion. In summary, the low-frequency impedance modulus of the composite coating gradually increases after doping with BTA-SiO₂@h-BN, and the best performance is observed when the addition is 25 wt%.

Fig. 9(a3-f3) presents the phase angle diagrams for the composite coatings over the test period. The width of the platform approaching “-90°” indicates the corrosion resistance of the coating; a broader platform suggests a better performance. Initially, all composite coatings doped with BTA-SiO₂@h-BN exhibit barrier properties after being soaked, implying that the corrosive media have not yet permeated the coatings and, consequently, the tested steel plate remains uncorroded [55]. At this stage, the phase angle maintains a constant state. However, the AEP-Dispersion-based coating demonstrates an almost negligible platform over the test period, indicating poor corrosion resistance. With an increasing dosage of the doping nanosheet, the composite coatings exhibit a more pronounced platform. Observed from the entire testing process, BTA-SiO₂@h-BN-EP-25 displays the most optimal anti-corrosion properties.

(iv) Salt spray test

Finally, a salt spray test was conducted to corroborate the results of the electrochemical tests. As shown in Fig. 10, it illustrates the digital images for various composite coatings on the steel plate during the salt spray test. After being exposed in salt spray environment for 240 h, the coatings displayed varying degrees of damage [55,56]. The scratch on the BTA-SiO₂@h-BN-EP-25 revealed only a minimal amount of corrosion products, whereas the AEP-Dispersion-based coating experienced relatively severe corrosion morphology, which spread around and caused the coating to peel off. In general, the ranking order for corrosion resistance from highest to lowest was observed as follows: BTA-SiO₂@h-BN-EPs-25 > 20 > 15 > 10 > 5, and AEP-Dispersion-based coating. This finding aligns with the results obtained from electrochemical testing. As described above, the lamellar structure of h-BN inhibits the penetration of corrosive media, and the adsorbed corrosion inhibitor BTA can chelate with metal ions to form a passivation film [57]. The combined effect of these two factors can significantly enhance the anti-corrosion properties of the composite coating, ensuring good performance in practical applications.

As shown in Fig. 11, the lamellar structure of h-BN inhibits the penetration of corrosive media, and the adsorbed corrosion inhibitor BTA can chelate with metal ions to form a passivation film. The combined effect of these two factors can significantly enhance the anti-corrosion properties of the composite coating, ensuring good performance in practical applications.

4. Conclusion

In this study, novel BTA-SiO₂@h-BN composite nanosheets were prepared through a simple physical dispersion method, which were then add to the aqueous epoxy dispersion to prepare the composite coatings. From the analysis of FESEM, the silica sol encapsulates the h-BN nanosheets, forming an irregular bubble-like morphology, which inhibits the aggregation of h-BN nanosheets within the composite coating. The composite nanosheets can construct a reticular structure within the coating, which is conducive to enhance the anticorrosive and thermal conductivity properties of the composite coating. The hydrogen bonding effect of the silica sol also aids in improving the mechanical properties

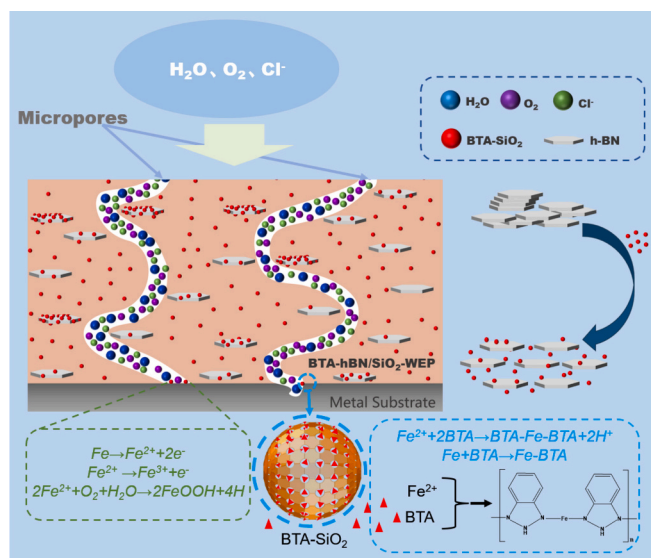


Fig. 11. Corrosion protection mechanism diagram of BTA-SiO₂@h-BN/EP composite coating.

and wear resistance of the coating. The porous structure of the silica sol effectively adsorbs the corrosion inhibitor BTA, thereby enhancing the corrosion resistance of the composite coating. Under the designed formulation, the composite coating system gradually increases with the rise in the content of composite nanosheets. When the relative content of the added BTA-SiO₂@h-BN reaches 25 % by weight, the cured composite coating exhibits optimal performance, indicating promising application in the field of functional anticorrosive coatings.

CRediT authorship contribution statement

Jinbiao Wang: Investigation. **Xiaomei Wang:** Conceptualization. **Xin Sun:** Formal analysis. **Xiao Wang:** Software. **Qiyuan Li:** Formal analysis. **Mingsheng Bu:** Visualization. **Lizhuang Chen:** Resources. **Zhengbai Zhao:** Investigation. **Hui Yan:** Writing – review & editing. **Weili Li:** Writing – original draft, 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2025.109309>.

Data availability

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

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