

Improved properties of epoxy composite coatings enabled by multi-dimension filler materials

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ABSTRACT

Nanofillers of various nano dimensions, ranging from 0D (such as SiO₂) to 1D (such as carbon nanotubes) and 2D (such as graphene), are commonly added to epoxy resin matrices to enhance their tribological properties, making them more suitable for various applications such as protective coatings, composites, and adhesives. Beyond solely utilizing single-nano-dimension fillers, 0D/2D multi-dimensional designed materials are more effective fillers for high-performance epoxy coatings due to their rich morphologies and chemistry. In this work, a highly anti-corrosive epoxy-based coating with multi-dimensional fillers of 2D hexagonal boron nitride (h-BN) and 0D mesoporous silica particles (mSi) is prepared and reported. The approach initially involved the sol-gel condensation reaction coating of h-BN sheets with mesoporous silica to obtain hBN@mSi multi-dimensional fillers. This was followed by the introduction of benzotriazole (BTA) as the corrosion inhibitor to hBN@mSi, forming BTA-hBN@mSi, which was later added to the epoxy resin to obtain the composite coating with improved performance. The underlying mechanism for the improved corrosion behavior in the modified epoxy was then explored using various methods. The results show that the increased specific surface area and pore volume of 0D/2D multi-dimensional fillers of hBN@mSi significantly increased in comparison to their single dimensions. This played a critical role in the BTA loading capacity in the filler and hence the anticorrosion performance of the modified epoxy coating. Furthermore, the modified epoxy coating exhibited good thermal conductivity and mechanical properties, making it suitable for various applications where corrosion resistance, thermal conductivity, and mechanical strength are key, such as in the construction of heat exchangers for various industries including chemical processing, oil refining, power generation, and HVAC systems.

1. Introduction

Epoxy resin is a crucial thermosetting polymer known for its excellent processability, strong chemical resistance, good insulation, and high adhesive properties [1]. Widely utilized in adhesives, electrical packaging, functional coatings, and other applications, epoxy-based coatings face two main challenges. Firstly, they tend to be brittle with low fracture toughness due to their high cross-link density after curing. Secondly, solvent volatilization during solidification in solvent-based epoxy coatings can lead to the formation of microholes or microcracks, reducing the coating's effectiveness as a corrosion barrier. In severe

cases, this can lead to the formation of local galvanic couples, exacerbating corrosion issues [2]. Doping nanoparticles into epoxy-based coatings is considered one of the many possible ways to overcome the named issues [3]. This is because nanoparticles, given their small size, unique surface and interface properties, and quantum size effect, are able to nanoscopically interact strongly with the epoxy creating improved performance seen at micro and macroscopic scales. The improved performance is seen as enhanced mechanical properties, heat resistance, and corrosion resistance of the nanocomposite coatings.

Nanoparticles are commonly categorized based on their shapes: 0D, 1D, and 2D. 0D nanoparticles include spherical metal oxide

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nanoparticles like SiO₂, TiO₂, Al₂O₃, and carbon black. 1D nanofillers, with diameters of less than 100 nm and lengths up to hundreds of nanometers, include nanotubes, nanowires, nanofibers, and nanorods. Additionally, graphene, h-BN, and nano clay are well-known 2D nanosheets. h-BN, often called “white graphene,” possesses non-permeability and a high specific surface area, along with excellent mechanical properties, thermal conductivity, wear resistance, barrier properties, and hydrophobicity [4–7]. However, due to the inert nature of the h-BN surface, surface modification is necessary to improve its dispersibility and optimize its interfacial compatibility within polymer resins when doping it into the polymer resins [8].

Beyond solely utilizing single-nano-dimension fillers, 0D/2D multi-dimensional designed materials with 0D nanoparticles (such as SiO₂ [9], TiO₂ [10], Fe₃O₄ [11], CeO₂ [12], ZrO₂ [13]) on the surface 2D nanosheets (such as GO [14], h-BN [15], MoS₂) are more effective fillers for high-performance epoxy coatings due to their rich morphologies and chemistry. For example, Liu et al. [16] synthesized a titanium dioxide-decorated graphene oxide nanocomposite using 3-aminopropyltriethoxysilane and modified it with g-(2,3-epoxypropoxy) propyltrimethoxysilane before introducing it into epoxy resin to form a modified epoxy coating composite tested on AA-2024 aluminum alloy. The modified coating demonstrated good anticorrosion properties and enhanced anti-UV aging performance. In another work, Zhong et al. [17] prepared reduced graphene oxide-silica nanocomposite fillers using a ball milling method followed by modification with silane coupling agent (KH-550) to ensure good dispersion in the coating, effectively prolonging the corrosion path and improving the corrosion resistance of the coating. Also, Wang et al. [18] synthesized a composite material with labyrinthine capillary pores by growing zinc molybdate *in-situ* on flaky h-BN using a hydrothermal method and added it as a filler into the resin matrix, significantly improving the anticorrosive properties of the modified coating. Our group has also contributed to this field [19], where we encapsulated mesoporous silica in ZSM-5 molecular sieves using a sol-gel method to form advanced fillers which were later introduced to epoxy coatings. The obtained composite coatings exhibited excellent corrosion resistance properties.

Learning from the previous reports, herein, we report the design and synthesis of 0D/2D multi-dimensional fillers based on 2D hexagonal boron nitride (h-BN) and 0D mesoporous silica particles (mSi) for improved epoxy coatings. Briefly, our approach involved an *in-situ* sol-gel condensation reaction for coating of h-BN sheets with mSi to obtain h-BN@mSi multi-dimensional fillers. Subsequently, benzotriazole (BTA) corrosion inhibitor was added to form BTA-h-BN@mSi. This mixture was then incorporated into the epoxy resin to produce a composite coating with improved performance. The modified epoxy coating broadly showed excellent corrosion resistance performance, good thermal conductivity, and mechanical properties, making it suitable for applications where these properties are broadly required such as in the construction of heat exchangers for various industries including chemical processing, oil refining, power generation, and HVAC systems.

2. Experimental section

2.1. Materials

h-BN (10–15 μm) was supplied by Shanghai McLean Biochemical Technology Co., LTD. Anhydrous ethanol (A.R.), concentrated hydrochloric acid (HCl), ammonium hydroxide, tetraethyl orthosilicate (TEOS), and cetyl trimethyl ammonium bromide (CTAB) were obtained from Sinopharm Chemical Reagent Co., Ltd. BTA was purchased from Guangzhou Fufei Chemical Technology Co., Ltd. Bisphenol-A type epoxy resin (E-44, epoxy value is 0.44 mol/100 g) was acquired from Jiangsu Sanmu Group, and the polyamide curing agent was purchased from Jinan Lingwei Chemical Co., LTD. Butyl acetate (BA, A.R.) was sourced from Jinan Yuanxiang Chemical Co., LTD. The defoaming agent YCK-670 was bought from Shanghai ICKE Chemical Co., LTD. The wetting

leveling agent BYK-333 and the wetting dispersing agent BYK-111 were obtained from Germany BYKE Chemical Co., LTD. Deionized water was prepared in-house.

2.2. Methods

2.2.1. Preparation of hBN@mSi

This was mainly done in three major steps. (1) 1 g h-BN, 1 g ammonium hydroxide and 1 g CTAB were dissolved in a mixed solution of 100 mL anhydrous ethanol and 8 mL deionized water which all were ultrasonicated for 30 min. Then the resultant solution was kept at 30 °C in a water bath under magnetic stirring for 10 min for full dispersion. The final solution is denoted Solution A. (2) During this, 9 g TEOS denoted as Solution B, was divided into 3 equal portions, and each was drop added slowly, to Solution A at predetermined intervals of 0 h, 2 h, and 4 h from the beginning of the reaction. After that, the resultant solution was stirred at a constant temperature (30 °C) for 6 h. This was followed by centrifuge washing with anhydrous ethanol, and vacuum drying at 50 °C for 24 h. The solid components obtained were silica-coated boron nitride denoted hBN@Si. (3) In the final step, the obtained powder was first ultrasonicated in hydrochloric acid-ethanol (1:10) solution for 30 min, then magnetically stirred at 70 °C for 6 h to remove the template agent, followed by filtering and washing with deionized water and anhydrous ethanol, and lastly drying at 40 °C for 24 h in vacuum. The final product was mesoporous silica-coated boron nitride powder denoted as hBN@mSi (mSi loading is approximately 0.4 g).

2.2.2. Introduction of BTA corrosion inhibitor to hBN@mSi

To load BTA into hBN@mSi, 0.5 g hBN@mSi particles were dispersed in a 50 mL ethanol/BTA solution (10 mg/mL). The mixture was stirred at room temperature for 12 h to facilitate the diffusion and loading of the BTA. Subsequently, the material was vacuum pressed for 3 h to fill the carrier pores. The filtered and washed material was then dried at 55 °C for 2 h, and ground to obtain BTA-hBN@mSi powder.

2.2.3. Fabrication of epoxy composite coating

First, epoxy resin was dissolved into BA to obtain a homogeneous mixture denoted Mixture A. Then, different amounts of BTA-hBN@mSi (0, 1, 5, 10 wt%) along with the dispersing agent (BYK-111) were doped into BA and stirred magnetically for 10 min to obtain a homogeneous mixture called Mixture B. In the next step, Mixture A and Mixture B were blended and stirred at a high speed (1000 rpm) for 30 min, the composite precursor denoted Solution C was obtained. Next, appropriate amounts of defoamer (YCK-670), and wetting and leveling agent (BYK-333) were added to Solution C. Polyamide 651 was used as the curing agent. Before being coated, the composite precursor Solution C and curing agent were blended and activated for 20 min.

To apply the coatings, the metal substrate had to be prepared as follows; the iron plate (tinplate version) and steel panels (Q235 steel) were first polished using metallographic sandpaper (P400, P600) and then washed with alcohol to remove dust. The activated composite precursor Solution C was then evenly coated on the plates using a rod coater. The film thickness was controlled around 90–120 μm.

Finally, the cured composite coatings were cured in an oven at 100 °C for 2 h to ensure complete curing. In the same way, pristine epoxy coating was also prepared according to the above method. The formulations for the preparation of composite coatings are presented in Tables S1–S4 in the supporting materials.

To study the influence of BTA-hBN@mSi on the properties of the cured coatings. Different contents of BTA-hBN@mSi (1, 5 and 10 wt%) were applied. For convenience, the obtained products were named M-Resin-X%, for modified resin with X wt% of BTA-hBN@mSi. For example, M-Resin-5 % is a composite coating with 5 wt% of BTA-hBN@mSi.

The schematic diagram summarizing the experimental methods for

the preparation of BTA-hBN@mSi nanoparticles and M-Resin-X% coatings is presented in Fig. 1.

2.3. Material characterization

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS10 FTIR spectrometer (Thermo Electron Corporation, USA) with an ATR diamond unit (Golden Gate). The thermostability was measured by thermogravimetric analysis (TGA, PerkinElmer) ranging from 25 to 800 °C at 10 °C/min under nitrogen atmosphere. X-ray diffraction (XRD) measurements were done on an XRD-6000 X-ray diffractometer (Shimadzu Corporation, Japan) at a voltage of 40 kV with Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) in the 2θ ranging from 5° to 90°. FESEM and EDS analyses were carried out on Merlin Compact microscope (Carl Zeiss, Germany) with a field emission gun to characterize the surface of the coatings and the element distribution. The adsorption rates and porosities of the obtained samples were analyzed by the ASAP 2000 (Micromeritics Instrument Corp.) particle testing system. During this test, the samples were pre-degassed at 150 °C for 5 h. The distribution curves of specific surface area and pore size were studied by the BET method and BJH method, respectively.

The mechanical properties of the coatings were tested as follows. The hardness property was tested by the pencil hardness method according to GB/T 6739-2006 standard. The toughness property was tested by a QTY-32 type paint film bending tester (Tianjin Weida testing machine factory) according to GB/T 1731-2020 standard. The impact resistance properties were conducted on the BGD 302 tubular paint film impactor according to GB/T 20624.2-2006 standard test. The tensile adhesion property was conducted by BGD500 type coating digital display tester (Sanfeng precision measuring instrument (Guangdong) Co., LTD) according to GB/T 5210-2006 standard.

The anti-corrosion properties of the coatings were tested using the following methods. First, a salt spray test was conducted using the YWX/Q-250 salt spray test chamber. Second, the electrochemical behavior of the dried coatings was studied using an electrochemical workstation

(VersaSTAT 3, Princeton Instruments) in a 3.5 wt% NaCl solution. In this test, the coated steel plate served as the working electrode, a platinum electrode (CE) as the auxiliary electrode, and a saturated calomel electrode (RE) as the reference electrode. The polarization curve was scanned at a speed of 2.5 mV/s over a range of -3 V to 3 V (relative to the open circuit potential), with a coated area of 9.6 cm². AC impedance testing was performed in the frequency range of 100 KHz to 0.01 Hz at an AC amplitude of 10 mV (relative to the open circuit potential). Third, X-ray Photoelectron Spectroscopy (XPS) broad spectra were obtained using an Axis Ultra DLDX model X-ray photoelectron spectrometer (Kratos, UK) to examine the coating's attachment failure surface.

The thermal conductivity of the coatings was tested using the LFA-467 Nano-flash thermal conductivity quantifier (NETZSCH Scientific Instruments Trading (Shanghai) Ltd.) and observed with images using the handheld HIKMICRO H36 infrared thermal imager. The samples were tested over a temperature range of 20 to 100 °C. The samples utilized were manually cut and shaped following the mold curing process, ensuring a consistent sample size.

3. Results and discussion

3.1. Synthesis and characterization of BTA-hBN@mSi

BTA-hBN@mSi samples were briefly prepared as follows (see Methods and Fig. 1a). hBN@mSi nanosheets were first obtained by coating silica particles on the surface of h-BN via the improved Stöber method [20] which involved the use of TEOS in hydrolysis-condensation reaction and CTAB as the templating agent. Subsequently, the residual template was removed by solvent extraction approach to obtain hBN@mSi whose structure contained hBN encapsulated by mesoporous silica. Afterwards, the corrosion inhibitor BTA was loaded onto the hBN@mSi to obtain the BTA-hBN@mSi which later was used as fillers to enhance the corrosion resistance of epoxy-based coatings (Fig. 1b).

The morphologies and structures of the prepared samples were characterized using FTIR, TG, XRD, SEM, and TEM methods (Fig. 2).

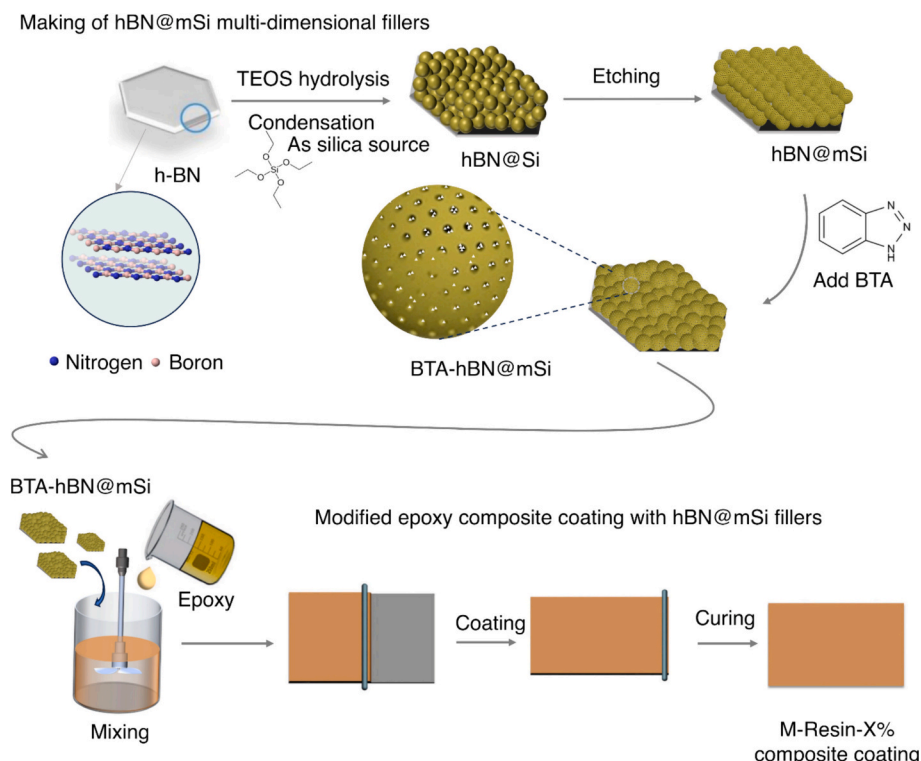


Fig. 1. Simplified schematic depicting the preparation of BTA-hBN@mSi fillers and its modification of the epoxy resin for a composite coating.

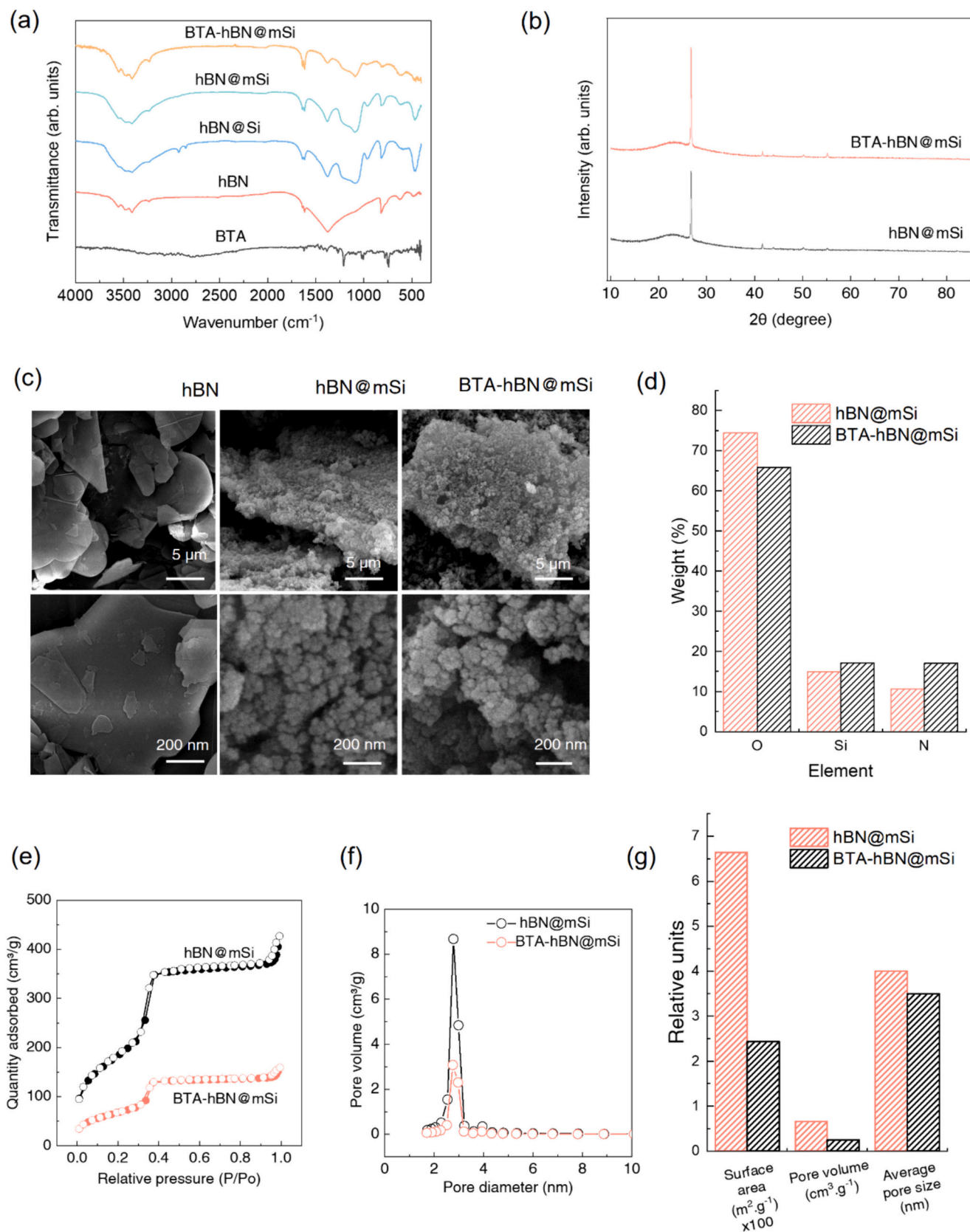


Fig. 2. Characterization of BTA-hBN@mSi. (a) FTIR plots of BTA-hBN@mSi and intermediates in the preparation process (including hBN, BTA, hBN@Si, and hBN@mSi). (b) XRD patterns of hBN@mSi and BTA-hBN@mSi depicting minimal interference in the phase structure of hBN@mSi caused by the presence of BTA. (c) FESEM images of hBN, hBN@mSi, and BTA-hBN@mSi with their zoomed profiles. (d) Summarized plot for the percentage of oxygen (O), silicon (Si) and nitrogen (N) in hBN@mSi and BTA-hBN@mSi samples from EDS. (e) N_2 adsorption and desorption isotherms curves, (f) pore size distribution and (g) summary of the specific surface area and pore size distribution of hBN@mSi and BTA-hBN@mSi samples.

First, the BTA-hBN@mSi and intermediates in the preparation process (including hBN, BTA, hBN@Si, and hBN@mSi) were studied with FTIR (Fig. 2a). In hBN and hBN-containing samples, two strong characteristic peaks at 814 cm^{-1} and 1376 cm^{-1} can be observed, which correspond to the tensile vibration of in-plane B–N and the bending vibration of out-of-plane B–N–B, respectively. In BTA-hBN@mSi, hBN@Si, and hBN@mSi, a characteristic absorption peak at 1093 cm^{-1} is attributed to the tensile vibration of Si–O–Si, while the absorption peak at 963 cm^{-1} is due to the deformation vibration of the Si–OH bond. Overall, hBN@Si retained all the characteristic peaks of BN and silica, signifying the successful decoration of silica nanoparticles on hBN nanosheets. The peaks at 2853 cm^{-1} and 2924 cm^{-1} in hBN@Si are due to the asymmetric and symmetric C–H stretching vibrations, respectively, stemming from CTAB templating and are seen to disappear in hBN@mSi spectra, signifying the formation of mesoporous silica upon the complete removal of CTAB. Furthermore, by comparing the spectra of pure BTA and BTA-hBN@mSi, the characteristic peak of BTA near 743 cm^{-1} related to the substituents of the adjacent benzene ring, can be observed, signifying the presence of BTA in BTA-hBN@mSi. Also, characteristic peaks at 1556 cm^{-1} , 1539 cm^{-1} , and 1456 cm^{-1} corresponding to the C=C tensile vibration on the benzene ring are observed in BTA-hBN@mSi, similar to BTA further confirming the presence of BTA in BTA-hBN@mSi.

The TGA curves of the prepared hBN@mSi and BTA-hBN@mSi particles are depicted in Fig. S1. The rapid weight loss observed in the range of 25 to $100\text{ }^{\circ}\text{C}$ for hBN@mSi is attributed to the escape of adsorbed water molecules from the pores. As the temperature increases, the curve gradually flattens out, with a mass loss of approximately 6 % at $800\text{ }^{\circ}\text{C}$, indicating excellent thermal stability of hBN@mSi particles. In contrast, for BTA-hBN@mSi particles, a gradual decrease in weight is observed within the range of 25– $800\text{ }^{\circ}\text{C}$. The initial weight loss before $200\text{ }^{\circ}\text{C}$ is primarily due to volatilization of adsorbed water, while after $200\text{ }^{\circ}\text{C}$, a distinct rapid decline can be attributed to gradual decomposition of BTA. At $800\text{ }^{\circ}\text{C}$, total weight loss for BTA-hBN@mSi particles amounts to about 16 %. These results demonstrate that in prepared BTA-hBN@mSi particles, BTA can be adsorbed not only on the surface but also within mSi pores.

To analyze the interference of the presence of BTA on the phase structure of the hBN@mSi in BTA-hBN@mSi, XRD was utilized (Fig. 2b). From the hBN@mSi and BTA-hBN@mSi XRD patterns, these both show characteristic X-ray diffraction peaks at $\sim 26.7^{\circ}$ and 42.8° which corresponds to (002) and (100) planes of layered hBN [7,21]. These are typical peak patterns associated with the layered structures of hBN nanosheets. The broad peak 23° is a characteristic amorphous SiO_2 peak, indicating that the silica seats around h-BN and in amorphous form. As noted, even after loading BTA to hBN@mSi no noticeable changes in the XRD patterns were observed which meant that BTA was simply adsorbed in the pores of mesoporous silica and does not change the structure and morphology of the hBN@mSi. To collaborate with the XRD results, FESEM imaging was employed to study the surface and internal morphology of the different hBN nanosheets at different stages of the preparation process (Fig. 2c). Before any modification of hBN, the microscopy images revealed clear 2D morphology of hBN nanosheets with relatively smooth surface. The porous structure of mSi in the hBN@mSi samples was verified by the TEM photograph (Fig. S2). It is important to note that the presence of h-BN particles leads to a competition between h-BN surface nucleation and mSi nucleation. However, due to the significantly lower free energy associated with forming a surface on a growing nucleus compared to homogeneous nucleation, heterogeneous nucleation is more likely to occur. Therefore, mSi generated primarily occurs on the BN surface, while scattered mSi remains in the minority. For the hBN@mSi and BTA-hBN@mSi images, they depicted a relatively indistinguishable composite structure with nanometer-scale OD powders of silica seated on the surface of h-BN nanosheets. Notably, the nano-sized silica coating formed on hBN surfaces were dense, uniform, with complete coverage which effectively changed the surface morphology of

h-BN. Despite similar morphology for both hBN@mSi and BTA-hBN@mSi, EDS results in Fig. 2d revealed that the N element increased significantly for the BTA-hBN@mSi, which can be directly attributed to the introduction of BTA in the pores of mesoporous silica.

To further elucidate the structure of mesoporous silica and the influence of the filled corrosion inhibitor BTA in hBN@mSi, we evaluated the specific surface area and porosity of hBN@mSi and BTA-hBN@mSi using N_2 adsorption-desorption isotherm analysis (Fig. 2e–f). Both obtained isotherms from hBN@mSi and BTA-hBN@mSi depicted typical type IV isotherms accompanied by hysteresis loops, indicating ordered mesoporous material structures in the two samples with pore diameters between 2 and 50 nm (Fig. 2f) [22,23]. However, hBN@mSi showed an H1 type hysteresis loop, often associated with porous materials consisting of almost uniform agglomerated spheres with a narrow pore-size distribution. Loading BTA in BTA-hBN@mSi changed the hysteresis loop to H3 type, commonly observed because of slit-shaped pores, directly indicating that the internal structure of the micropores was irregular. These results confirm that after etching, we successfully obtained uniform mesoporous silica, and then on loading BTA, the process led to funnel-shaped micropores with different shapes and sizes directly related to the non-uniform loading of BTA. This is directly confirmed in Fig. 2g, where we observe that the specific surface area of hBN@mSi is as high as $663.75\text{ m}^2\cdot\text{g}^{-1}$ but decreased significantly to $243.43\text{ m}^2\cdot\text{g}^{-1}$ when BTA is loaded in BTA-hBN@mSi. The same trend is observed for the pore volume, which decreased from $0.66\text{ cm}^3\cdot\text{g}^{-1}$ in hBN@mSi to $0.25\text{ cm}^3\cdot\text{g}^{-1}$ in BTA-hBN@mSi due to the occupation of BTA. Furthermore, the average pore size distribution was narrowed from 4.0 nm to 3.5 nm, indicating that BTA is successfully absorbed and loaded into the mesoporous silica. Overall, the hBN@mSi large specific surface area and pore volume facilitated the uptake of BTA corrosion inhibitor which is expected to improve the corrosion performance of epoxy-based BTA-hBN@mSi.

3.2. BTA-hBN@mSi in epoxy composite coating

In this section, we introduce the incorporation of BTA-hBN@mSi into epoxy resin and investigate the properties of the resulting composite coating. Initially, BTA-hBN@mSi was added to pure epoxy to form an epoxy-based BTA-hBN@mSi composite coating. Subsequently, the composite coating was applied to iron and steel plates (For details see Methods). For comparative analysis, different amounts of BTA-hBN@mSi (1, 5, and 10 wt%) were added to the epoxy and examined. For ease of reference, the resulting products were labeled as M-Resin-X %, indicating modified resin with X wt% of BTA-hBN@mSi. For instance, M-Resin-5 % represents a composite coating containing 5 wt% of BTA-hBN@mSi.

Here, the surface and cross-section of the functional composite coatings were imaged with SEM to study and analyze their microstructure. The neat epoxy showed a smooth coating surface, whereas the introduction of fillers resulted in a relatively rough surface (Fig. 3a). Notably, despite the rough morphology of the BTA-hBN@mSi-filled epoxy, the composite coatings remained closely bonded with their macro surfaces flat and smooth, showing no obvious defects such as pores and cracks. This indicates that the added powder had good compatibility with the coating. The reason for this is that mSi nanoparticles were firmly anchored on the surface of hBN, which not only minimized the interaction between hBN particles but also ensured strong interfacial bonding between hBN and epoxy groups. Furthermore, hBN can serve as a “carrier” for mSi during the preparation process, further preventing molecular aggregation [8]. Fig. 3b shows the cross-section images of the coatings. With the presence of fillers, a fish scale cross-section was displayed, indicating a strong interaction between BTA-hBN@mSi and the epoxy resin matrix [24,25]. Notably, in the composite coatings with filler loadings of 1 % and 5 %, one can observe a close-knit union between the resin and the fillers that ensures durability and stability. However, when the loading reached 10 %, powder

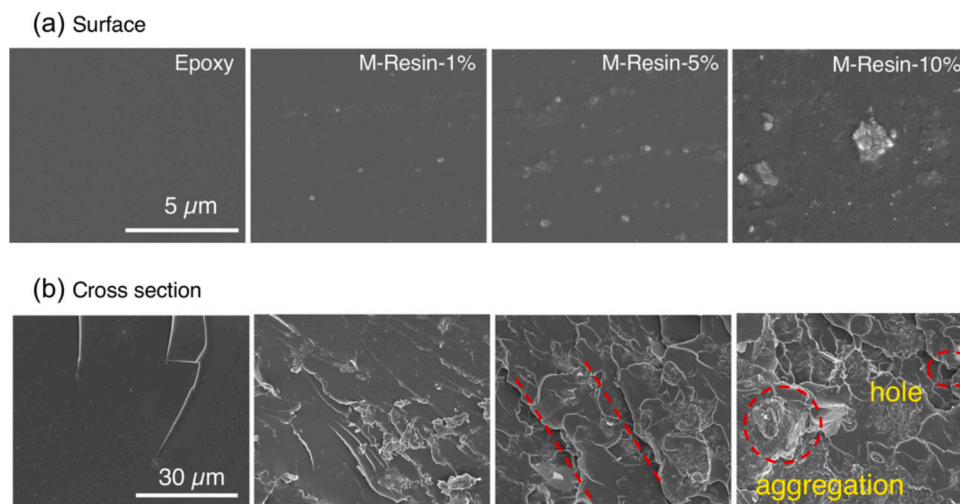


Fig. 3. Surface (a) and cross-section (b) FESEM imaging of coatings.

aggregation occurred, leading to coating defects such as holes, which impacted coating performance. Overall, the BTA-hBN@mSi powder acts as a crucial component in conferring enhanced anti-corrosion properties to the coating. Notably, the red dotted lines of the 5 wt% filler loading highlight a crucial aspect of this integration: the flake powder forms a multi-layer physical barrier within the coating. This barrier, often referred to as the “maze” effect, is a strategic defense mechanism against corrosion. It works by creating a complex, labyrinthine path for corrosive agents, thus significantly hindering their direct access to the metal matrix. This barrier effectively acts as a labyrinth that confuses and impedes corrosive elements, making it much more difficult for them to reach and attack the vulnerable metal surface.

3.3. Mechanical properties

Mechanical properties play a crucial role in the performance of coatings, determining their durability, adhesion, and overall effectiveness. These properties dictate the coating's ability to withstand various mechanical stresses, including abrasion, impact, bending, and stretching. Incorporating fillers into resins is a common and effective method for enhancing their mechanical properties. Table 1 illustrates how the mechanical properties (hardness, flexibility, shock resistance, and adhesion) of epoxy coatings varied with the content of BTA-hBN@mSi, ranging from 1 to 10 wt%. Generally, an increase in BTA-hBN@mSi loading resulted in improved coating hardness. However, flexibility and impact resistance showed a decreasing trend with an increased high loading of 10 wt%. Adhesion initially decreased with increasing BTA-hBN@mSi content, followed by a gradual increase. These observed trends are primarily influenced by the properties of the filler. The unique structure of the BTA-hBN@mSi powder filler plays a pivotal role in enhancing the mechanical properties of the coating. It effectively fills the defects in the resin matrix, bridging gaps or voids and improving adhesion, albeit with a slight decrease in flexibility. Additionally, the mesoporous structure of the silica grown *in-situ* on the surface of the hBN

Table 1

Mechanical properties of neat epoxy, M-Resin-1 %, M-Resin-5 %, and M-Resin-10 % coatings.

	Epoxy	M-Resin-1 %	M-Resin-5 %	M-Resin-10 %
Hardness	2H	2H	3H	3H
Flexibility (mm)	0.5	0.5	1	1
Impact resistance (kg. cm)	50	50	50	45
Adhesion (MPa)	2.01	1.57	2.18	2.25

sheet creates a rivet effect with the resin matrix. This interaction strengthens the bond between the epoxy matrix and BTA-hBN@mSi, resulting in a more cohesive and durable coating. Furthermore, the Si-OH group of mesoporous silica and the cured epoxy resin can form hydrogen bonds, restricting the migration of polymer chains and increasing the coating's hardness and adhesion properties [1,26]. Based on this analysis, M-Resin-5 % demonstrates a better-balanced performance in terms of mechanical properties.

3.4. Thermal conductivity of composite coating

Thermal conductivity is a crucial property in coatings as it enables efficient heat transfer, preventing overheating in electronic devices and industrial equipment. In this study, we investigated the thermal conductivity of our composite coatings using infrared thermal imaging experiments (Fig. 4). The results showed that as the content of BTA-hBN@mSi filler increased, the surface temperature of the coatings rose more rapidly (Fig. 4a–b). For instance, at 50 s, the surface temperature increased from 63.0 °C for the neat epoxy coating to 73.5 °C, 87.1 °C, and 95.6 °C for the M-Resin-1 %, M-Resin-5 %, and M-Resin-10 % coatings, respectively. For M-Resin-10 % with the best thermal conductivity, in order to better understand its changes, a more comprehensive infrared thermal imaging change diagram is provided in Fig. S3. Additionally, the thermal conductivity of the composite coatings improved with increasing BTA-hBN@mSi loading, as evidenced by the qualitative analysis presented in Fig. 4c. For example, the thermal conductivity of the M-Resin-5 % coating increased by approximately 50 % compared to that of the neat epoxy coating, highlighting the significant role of the fillers, particularly hBN, known for its excellent thermal conductivity [27].

3.5. The corrosion resistance of composite coating

In this section, we investigate the effect of BTA-hBN@mSi on the corrosion properties of the modified coating. The different modified resin samples were coated and cured on the test steel plate and then immersed in 3.5 wt% NaCl solution (see Methods). Tafel polarization curves and AC impedance spectroscopy were initially utilized to study the associated corrosion performance and later the associated mechanisms investigated with XPS analysis.

First, Tafel polarization results were obtained after immersing the coated plate in a 3.5 wt% NaCl solution for 40 days. Fig. 5a illustrates the Tafel polarization curves of the different composite coatings with BTA-hBN@mSi loading ranging from 0 to 10 wt%. These results are summarized in Fig. 5b–c, where β_a (in mV) and β_c (in mV) represent the

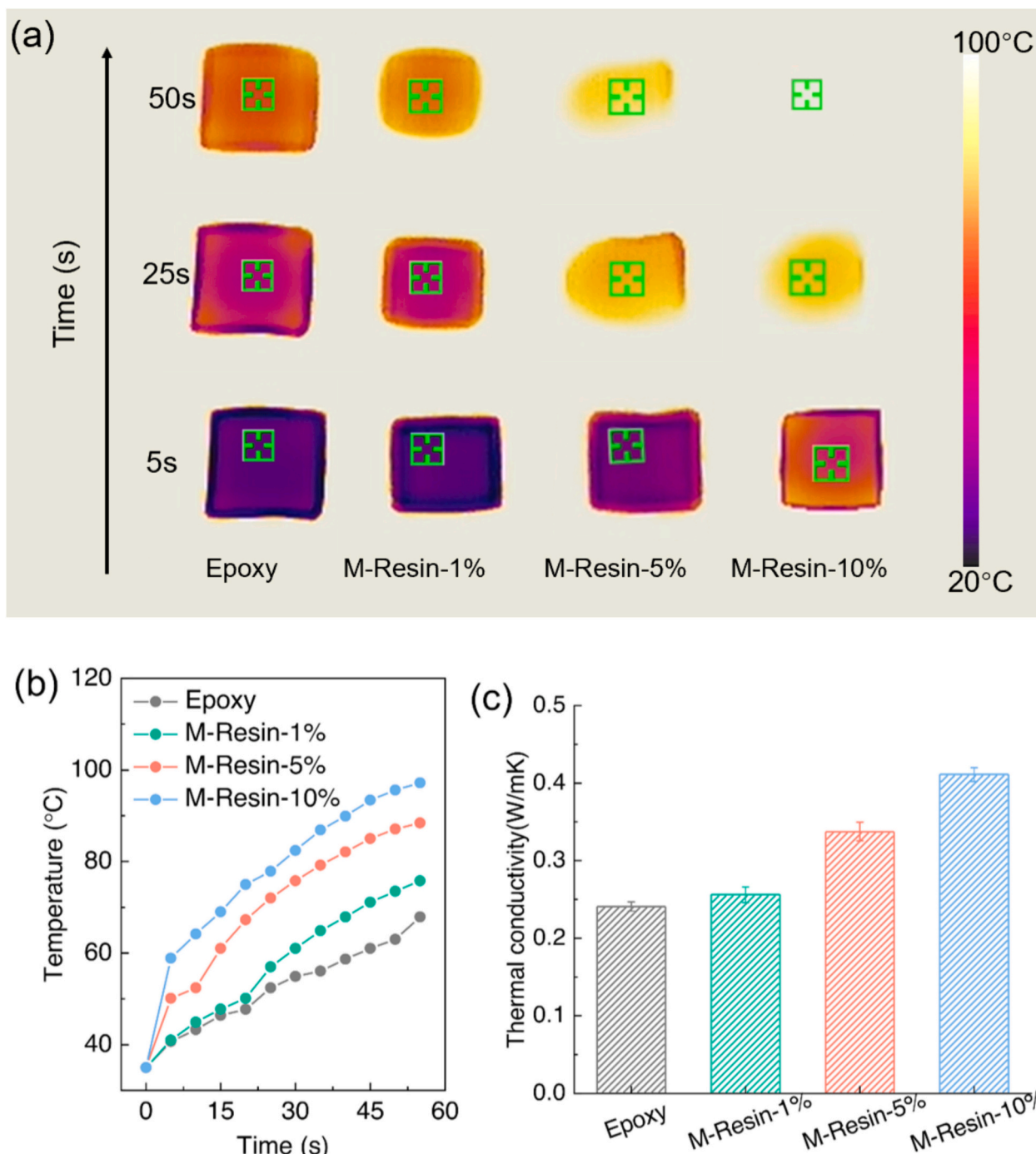


Fig. 4. Thermal conductivity of composite coating. (a) The infrared thermal images of composite coatings with different BTA-hBN@mSi filler loading (0, 1, 5 and 10 wt%). (b) The surface temperature variation of composite coatings versus testing time. (c) Thermal conductivities of coatings as the functions of BTA-hBN@mSi filler loading in the composite coatings.

anode and cathode Tafel slopes, respectively. The corrosion rate (C.R) can be calculated using Tafel polarization data and Eq. (1) [28–31]. The equation relates I_{corr} to C.R and the various constants as follows: where K is the corrosion rate constant ($3.27 \text{ mm} \cdot \text{g}/(\text{A} \cdot \text{cm} \cdot \text{year})$), I_{corr} represents the corrosion current density (A/cm^2), ρ represents the density of carbon steel ($7.87 \text{ g}/\text{cm}^3$), and E_w represents the equivalent weight of carbon steel (27.92 g). The data reveal a gradual decrease in I_{corr} of the coating from $3.644 \times 10^{-8} \text{ A}/\text{cm}^2$ to $2.28 \times 10^{-11} \text{ A}/\text{cm}^2$, accompanied by a reduction in C.R (in mm/year) as the BTA-hBN@mSi loading increases from 0 % to 10 % (Fig. 5c). BTA effectively impedes both the anodic and cathodic reactions by chelating with metal substrate cations, forming

insoluble complexes around the anode region and creating a stable inert protective layer, thereby reducing the corrosion rate of steel [32]. The 2D hBN fillers play a crucial role in prolonging the access of the corrosive medium to the steel surface, while the covalent bond between the 2D filler and epoxy resin enhances the coating density, resulting in better metal protection. However, an excess of BTA-hBN@mSi, as observed in the M-Resin-10 % composite coating, may lead to poor encapsulation of the resin around the filler due to a misalignment in surface energy, resulting in voids within the coating. This compromises its protective properties and increases the self-corrosion rate of the coating. Optimal anticorrosion performance was observed when the

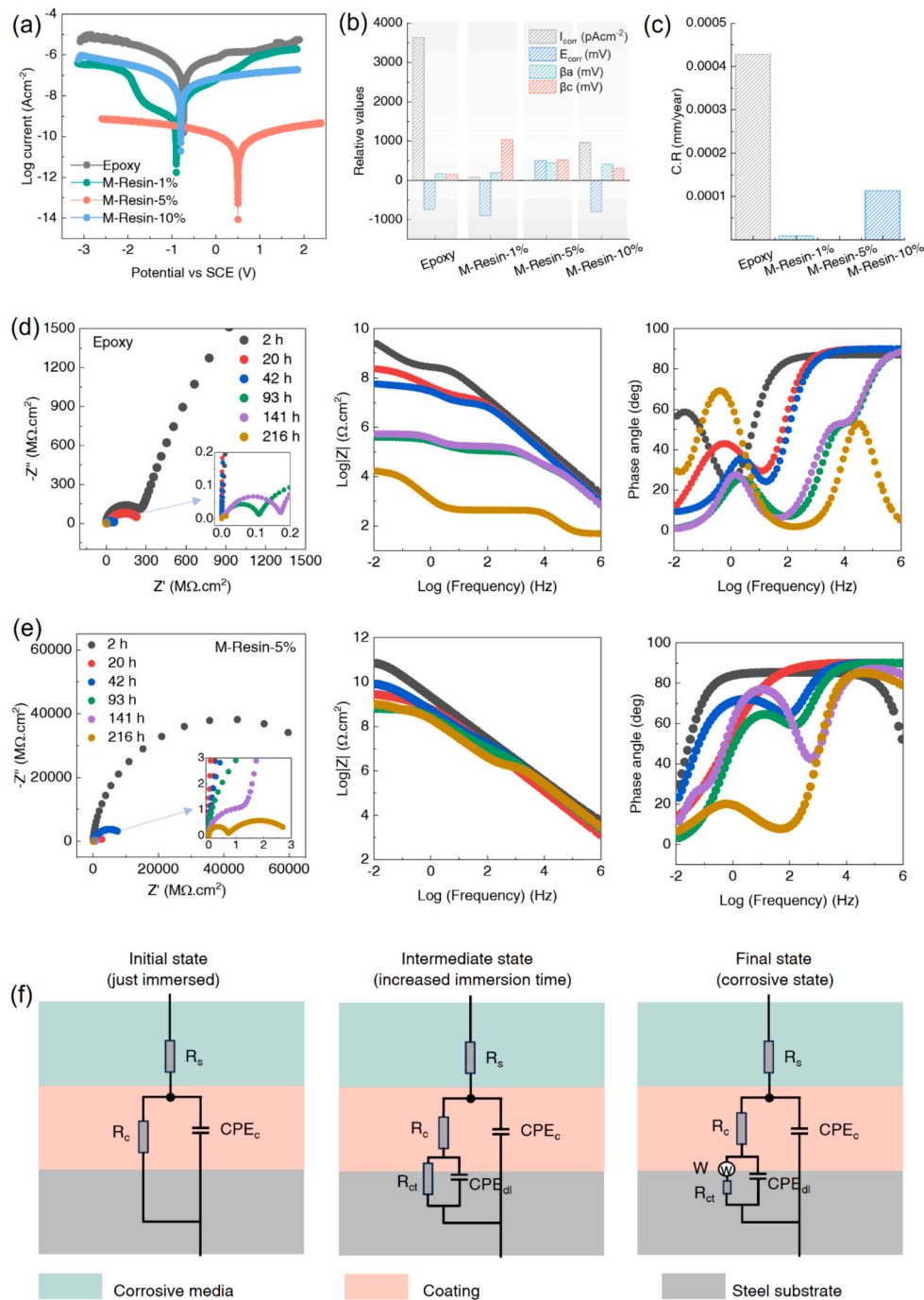


Fig. 5. The corrosion resistance of composite coatings. (a) Comparison of polarization curves of neat epoxy and composite coatings with different BTA-hBN@mSi filler loading in 3.5 wt% NaCl aqueous solution for 40 days. (b–c) Summary of the corrosion parameters of coatings from (a). (d–e) Nyquist plots, Bode plots, and Phase plots of neat epoxy and M-Resin-5 %. For M-Resin-1 % and 10 %, see Figs. S4–5. (f) Models for the equivalent circuit of the composite coating in 3.5 wt% NaCl solution.

BTA-hBN@mSi content was set at 5 %.

$$C.R = K \frac{I_{corr}}{\rho} E_w \quad (1)$$

Next, EIS measurements were carried out to gain a deeper understanding of the anti-corrosion mechanism of composite coatings during the corrosion process across a time duration of 216 h (Figs. 5d–e and S4–5). Again, steel substrates coated with the composite coatings having different loading of BTA-hBN@mSi were immersed in a 3.5 wt% NaCl solution and tested. Figs. 5d–e and S4–5, left depict the fitted Nyquist plots of the various coatings. Here, the diameter of the impedance arc is

directly indicative of the coating's corrosion resistance with a larger impedance arc diameter signifying superior corrosion resistance [33–36]. From the figures, the neat epoxy coating exhibited two-time constants (Fig. 5d) in the initial test phase, indicating that the corrosive media penetrated the coating's interior in few hours, leading to a soluble metal transfer from the steel surface to the electrolyte solution. However, coatings containing BTA-hBN@mSi fillers displayed one impedance arc. Notably, the M-Resin-5 % coating (Fig. 5e, left) displayed the largest impedance arc radius, illustrating its remarkable corrosion resistance. As the immersion time progressed, a noticeable decrease in the impedance radius arc was observed, indicating a gradual

decline in corrosion resistance over time. The results were confirmed by their respective Bode plots (Figs. 5d–e and S4–5, middle). These plots, showing the low-frequency impedance modulus ($|Z|_f = 0.01$ Hz), serve as semi-quantitative indicators for assessing the resistance of the coating to corrosive media. The M-Resin-5 % composite coating exhibited a $|Z|$ value decrease from 10^{11} to 10^9 after 216 h of soaking, indicating superior long-term corrosion resistance and stability compared to other formulations. The higher the value, the better anti-corrosion properties of the coating [18,37]. Additionally, phase diagrams (Figs. 5d–e and S4–5, right) provided insight into the coatings' corrosion resistance over time, with wider platforms close to “ -90° ” indicating better performance [36]. M-Resin-5 % maintained a relatively wide platform throughout the 216 h testing period, confirming its excellent and stable anti-corrosion properties. Overall, the addition of fillers improved the corrosion resistance of the epoxy, with M-Resin-5 % (5 wt% loading of BTA-hBN@mSi filler) showing superior corrosion resistance compared to formulations with 1 wt% and 10 wt% loading. This suggests that the optimal loading of BTA-hBN@mSi filler is 5 %. Excessive filler loading can lead to poor embedding in the polymer matrix, resulting in the formation of voids in the coating, accelerating the penetration of corrosive media. And, if the content of the BTA-hBN@mSi is small, the filler cannot form a labyrinth effect in the coating system.

To further provide an understanding into the anti-corrosion behaviors of the composite coating, the equivalent electrical circuits (EEC) of the composite coating at different corrosion stages were analyzed (Fig. 5e) [38]. In the figure, R_s and R_c represent the solution resistance and micropore resistance of the coating surface, respectively. R_{ct} signifies the charge transfer resistance, CPE_c is the coating capacitance, CPE_{dl} stands for the constant phase angle element during metal corrosion, and W represents the Warburg impedance [39,40]. Generally, the corrosion process occurs in two main stages. In the initial stage (Fig. 5f, left), the corrosion medium gradually infiltrated into the coating via inherent micropores, serving as channels, but it did not reach the metal surface at this point. In the second stage, the corrosion medium gradually penetrated the metal surface (Fig. 5f, middle) and later accumulated corrosion activity at the interface (Fig. 5f, right) between the metal and the coating. The latter stage is paramount in determining the composite coating's anti-corrosion performance. To explain the above observations, we looked at penetration of the corrosive medium increased with immersion time seen as two-time constants for all the coatings. The high-frequency time constant was determined by R_c and CPE_c , while the low one was determined by R_{ct} and CPE_{dl} . The emergence of R_{ct} and CPE_{dl} signaled the second stage of corrosion. In the second corrosion phase, initially, the Nyquist plots of both neat epoxy and composite coatings could be fitted using model in Fig. 5f, middle. However, with the increased test time, the Nyquist plots of neat epoxy coatings were better fitted with model in Fig. 5f, right. This indicated that as the corrosive material accumulated, the epoxy coating on the steel surface gradually became loose, thereby facilitating the penetration of the corrosive medium and forming a Warburg impedance element [41]. The result suggested that the corrosive medium diffused at the interface between metal and coating, leading to a sharp decline in the coating's corrosion resistance. In M-Resin-X% coatings, the released anions of BTA can form stable complexes with the cations of the metal, which are adsorbed on the metal surface to form CPE_c and R_c . In addition, the inherent physical barrier effect of the 2D material itself can delay the penetration of the corrosion medium [42]. Consequently, the composite coating exhibits a Warburg impedance element only after a longer immersion period. Its equivalent circuit still aligns with model in Fig. 5f, middle, indicating that the doped coatings have superior corrosion resistance property.

The EIS test results were fitted using the EEC models, facilitated by the ZsimpWin software. Table S5 presents the fitting values of key relevant parameters subsequent to a 216 h immersion period. Notably, R_c serves as a crucial indicator for assessing the compactness of the film, whereas R_{ct} reflects the anticorrosion efficacy of the metal substrate. To gain further insights into the long-term corrosion resistance of the

composite coating, a comparative analysis was conducted on the R_c and R_{ct} values of coatings fortified with varying filler additions, post-long-term soaking. As depicted in Fig. S6, subsequent to a 216 h immersion period, the R_c and R_{ct} values of the M-Resin-5 % coating exhibited a marked increase, spanning 3–4 orders of magnitude compared to the epoxy coating. This substantial enhancement signifies that the coating fortified with this specific filler content boasts superior long-term protection capabilities, which aligns perfectly with the analysis outcomes presented in the Bode diagram of Fig. 5. Consequently, it underscores a substantial improvement in the corrosion resistance of the composite coatings compared with Epoxy. Furthermore, this finding underscores the pivotal role that coating density plays in determining its corrosion resistance properties.

To pinpoint the role played by the BTA inhibitor, XPS was utilized to analyze the bonding type of the inhibitor molecules adsorbed on the surface of the matrix. Fig. 6a displays the comprehensive XPS spectrum of the electrode surface, while Fig. 6b–e provides a closer look at the XPS fine spectra for the C, Fe, N, and O peaks, respectively. Particularly, Fig. 6e clearly shows the Fe 2p spectrum at 711.2 eV and the Fe_2O_3 peak at 725.0 eV, indicating that BTA can safeguard the metal from excessive oxidation of steel [43]. Additionally, the N 1s spectrum on the substrate, following immersion in a simulated artificial seawater solution containing 3.5 wt% NaCl, is shown in Fig. 6d. The peaks at 399.92 eV and 401.20 eV represent $=N-$ and $N-Fe$ bonds, respectively [44–48], verifying that BTA inhibitor molecules had been successfully adsorbed onto the surface of the steel substrate. Here, N atoms can serve as the active

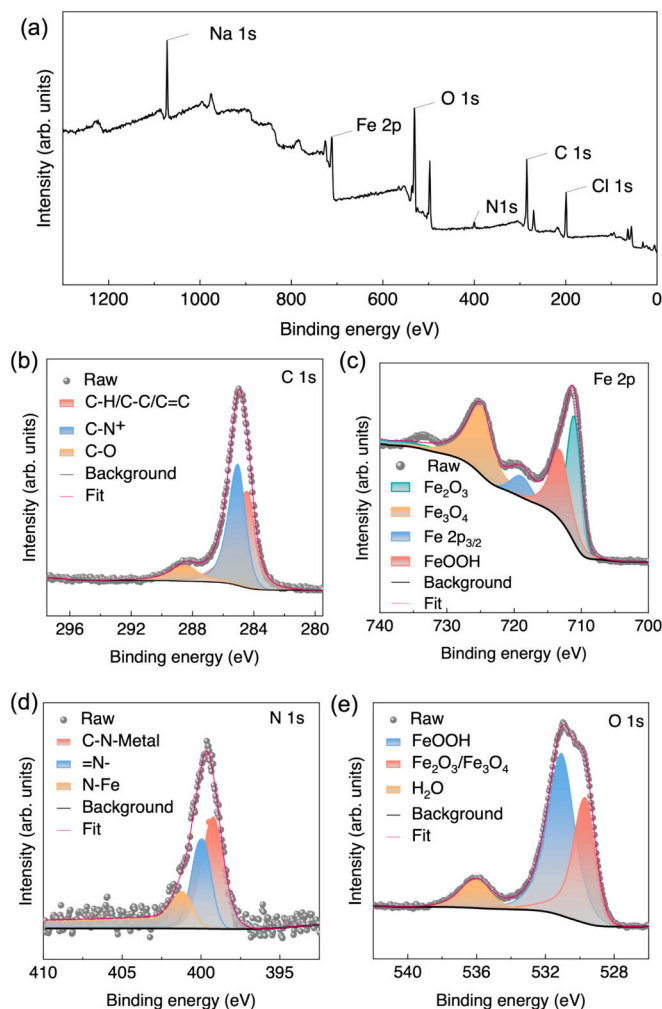


Fig. 6. XPS Survey and relative high-resolution spectra from Q235 steel surface adsorbed with BTA-hBN@mSi-based epoxy including C 1s, Fe 2p, N 1s and O 1s.

center and react with the iron atoms in the electrode to form a passivation film on the steel's surface, thereby protecting the steel matrix [49]. These results also align well with the results from the electrochemical tests. Moreover, the result also suggests that the complexes produced by the chelation of anions in BTA with metal cations can be adsorbed on the metal surface and enhance the adhesion of composite coatings [50].

Finally, we visually assessed the corrosion resistance of the composite coatings on steel plates, as shown in Fig. 7. The visual analysis strongly supported the corrosion electrochemical test results, with M-Resin-5 % demonstrating the best performance in terms of metal protection after 300 h of exposure to saline corrosion. Surface corrosion in the case of M-Resin-5 % was minimal and spread evenly along the split to both sides. Overall, the performance ranking was as follows: M-Resin-5 % > M-Resin-10 % > neat epoxy > M-Resin-1 %.

Overall epoxy modified with 5wt% BTA-hBN@mSi filler is a superior corrosion-resistant coating which is capable of doing so according to the proposed corrosion protection mechanism in Fig. 8. The mechanism follows three different major approaches; the physical barrier creation, corrosion inhibitor effect and oxygen capture effect and are explained as follows. This synergistic effect between the three hinders both cathodic and anodic reactions, ultimately enhancing the corrosion resistance of the composite coating.

- (1) *The physical barrier creation.* The physical barrier of mesoporous silica, h-BN, and epoxy at the beginning of impregnation is imperative to inhibit the diffusion of aggressive substances such as O_2 , Cl^- , and water. By introducing BTA-hBN@mSi as a pore filler, the inherent vulnerabilities of the pristine epoxy are effectively sealed, thereby enhancing both the compactness and bonding strength of the coating. Furthermore, the unique “maze” structure of the BTA-hBN@mSi composite offers a non-straight “brick-layer” interrupted path for aggressive substances and hence not getting fast to reach the steel matrix, thus bolstering its physical barrier properties. In addition, the residual microporous structure of mesoporous silica aids in the competitive adsorption of Cl^- from the electrolyte solution, further minimizing the diffusion of aggressive substances.

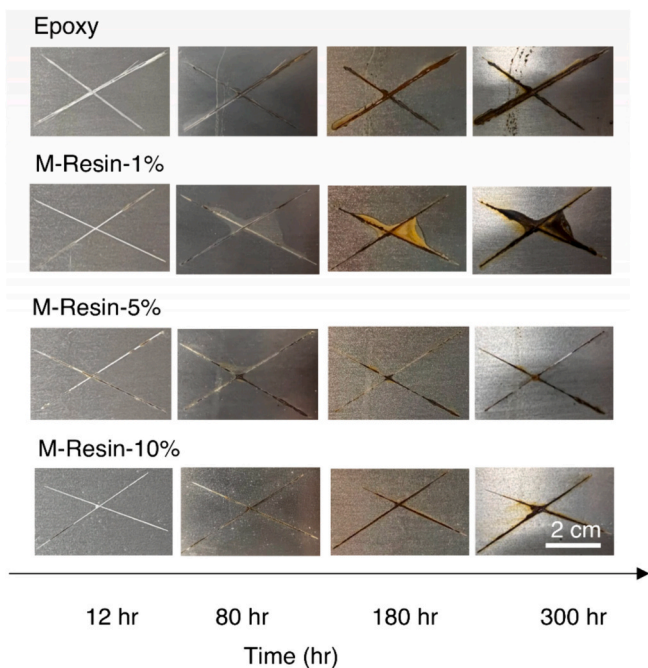


Fig. 7. Optical image surface analysis of the different coatings after exposure to saline corrosion for 300 h.

- (2) *Corrosion inhibitor effect.* Then as the immersion time progresses, corrosive substances penetrate the steel matrix, leading to initial corrosion on the steel surface. But due to the integration of mesoporous silica which has a high specific surface area along with dense pore channels in BTA-hBN@mSi modified epoxy, the mSi can effectively act as a carrier for the corrosion inhibition. And in the case of any coating damage, mesoporous silica helps to stimulate the reaction to release the corrosion inhibitor BTA through an active or passive mechanism, which can chemically bind to the steel matrix surface to form a protective film that not only repairs the coating but also provides an extra barrier.
- (3) *Oxygen capture effect.* Due to the unique combination of B—O bonds, h-BN is capable of trapping oxygen molecules and preventing their infiltration into the metal matrix when exposed, thereby suppressing the cathodic reaction [51,52]. This synergistic effect hinders both cathodic and anodic reactions, ultimately enhancing the corrosion resistance of the composite coating.

4. Conclusion

In this work, we presented a simplified and cost-effective method for modifying epoxy coatings with multi-dimensional fillers consisting of 2D h-BN nanosheets and 0D mesoporous silica. The resulting composite coating, with optimized loading, demonstrated superior corrosion protection, thermal conductivity, and mechanical properties, making it suitable for all these various applications. To create these composite coatings, we utilized the sol-gel technique to directly grow mesoporous silica on the surface of h-BN nanosheets. We then introduced a BTA corrosion inhibitor to this hBN-decorated mesoporous silica creating a multidimensional BTA-hBN@mSi filler which was later added to epoxy to obtain the modified advanced composite coating. This process allowed us to take advantage of h-BN's excellent thermal conductivity and mesoporous silica's large surface area to load the BTA corrosion inhibitor. As a result, we obtained an epoxy-compatible composite filler that promoted uniform dispersion, reducing h-BN agglomeration and leading to superior composite coating performance. The composite coating showed improved corrosion protection compared to the neat epoxy coating due to its multi-protection mechanism. This mechanism includes the ability to create a physical barrier due to its unique non-straight “brick-layer” structure, which can interrupt the access of corrosion agents to the metal. Additionally, the presence of the BTA inhibitor allows for chemical binding to the steel matrix surface, forming a protective film that not only repairs the coating but also provides an extra barrier. Furthermore, the h-BN has an oxygen capture effect, trapping oxygen molecules and preventing their penetration onto the metal surface. The modified coating could be used to protect metals used in the construction of heat exchangers for various industries, including chemical processing, oil refining, and power generation.

CRediT authorship contribution statement

Weili Li: Writing – review & editing, Investigation. **Xiao Wang:** Writing – review & editing, Formal analysis. **Mingsheng Bu:** Investigation, Data curation. **Xin Sun:** Validation, Supervision, Resources, Methodology. **Zhengbai Zhao:** Visualization, Supervision. **Lixin Xu:** Visualization, Investigation. **Lizhuang Chen:** Writing – review & editing, Investigation. **Zhaolei Li:** Visualization, Supervision. **Mike Tebyetekerwa:** Writing – review & editing, Visualization, Validation, Supervision.

Declaration of competing interest

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

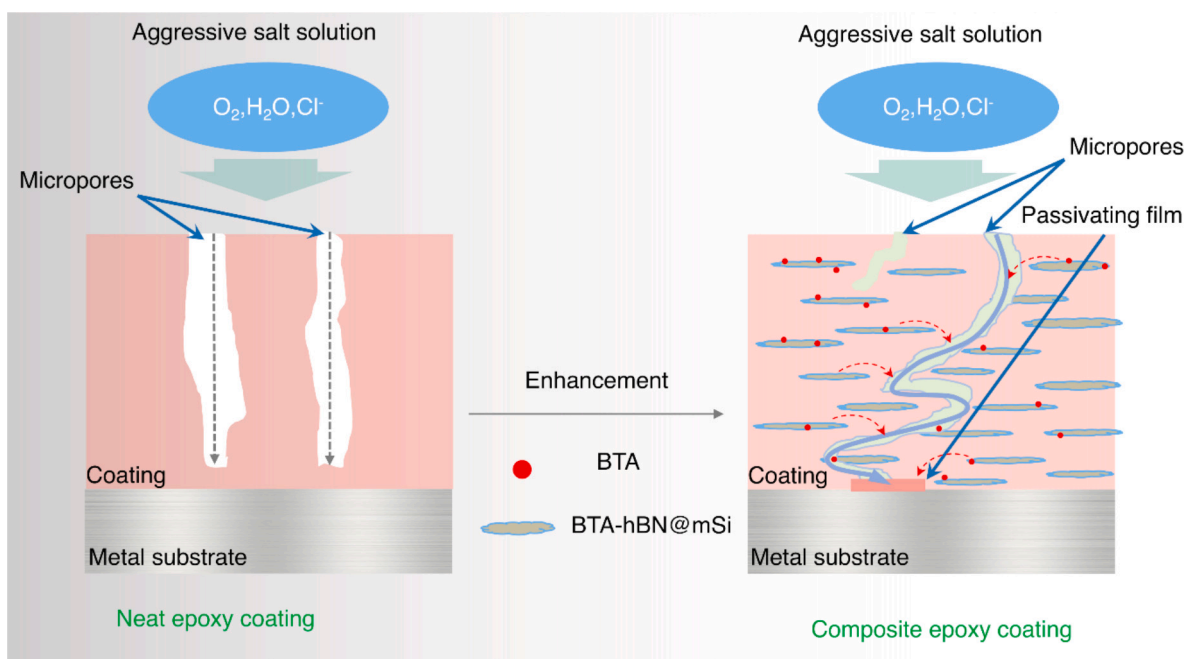


Fig. 8. Schematic diagram for proposed corrosion protection mechanism by the composite coating.

Data availability

Data will be made available on request.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2024.108800>.

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