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pH-Responsive Smart Polymer Nanocomposites for Anti-Corrosive Coatings

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Abstract

Metallic corrosion under adverse marine and industrial conditions imposes gigantic financial burdens and risks worldwide. Conventional waterproofing waterborne epoxy has passive barrier protection, but is also inherently microporous, lacking intrinsic repair ability against mechanical damage and thus rapidly decays. This is a critical gap that this work tries to bridge by designing a new pH-responsive hybrid polymer nanocomposite by using polyethyleneimine-tannic acid-cerium functionalized boron nitrate nanosheets with chitosan-capped mesoporous silica particles loaded with corrosion inhibitors in a water-borne epoxy matrix. The synergistic structure will enhance passive barrier properties through tortuous pathways created by two-dimensional nanofillers and active self-healing by means of pH-dependent on-demand release of corrosion-inhibitors in reaction to local acidity created upon the onset of corrosion. The electrochemical impedance spectrophotometry had revealed that the hybrid nanocomposite coating had a very high impedance modulus of the low frequency (9.8109 ohms/cm 2) of 75 days at low concentration (3.5 wt%) of NaCl solution, which is more than two orders of magnitude greater than the pure waterborne epoxy. In addition, the artificially scribed samples exhibited high healing properties under prolonged salt spray environments and corrosion proceeded very slowly even after 100 days in salt spray. Simulations with the help of molecular dynamics have confirmed the presence of much lower diffusion coefficients of water, oxygen and chloride ions and lower fractional free volume. These results compose scalable, environmentally benignant next-generation intelligent anticorrosive coating that can combine superior long-term barrier performance with autonomous active healing with enormous potential to increase the service life in problematic settings.

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INTRODUCTION

Corrosion is one of the most urgent problems of metallic infrastructure on the global level as it leads to losses in the economy of hundreds of billions of dollars annually, and to damage the integrity of the structures and environmental safety. Metallic structures like offshore platforms, ships, pipelines, bridges and petrochemical storage tanks are continuously subjected to aggressive electrolytes in harsh marine and industrial environments which promote electrochemical corrosion. The conventional organic coating, especially waterborne epoxy coating, has been used long as the main line of defense which forms a physical barrier against corrosive species. But these types of coatings naturally form during curing and service, and develop micropores and microcracks which permit ingress of water, oxygen, and chloride ions, eventually resulting in under-film corrosion. After mechanical damage, in conventional coating, there is no active repair mechanism and therefore the corrosion propagates quickly and the coating needs frequent maintenance.

To address these shortcomings, scientists have been investigating smart anticorrosive surfaces which integrate pH sensitive nanocontainers which can be used to release corrosion inhibitors on demand in response to local pH variations that indicate the occurrence of corrosion [1], [2]. Significant improvements have been made to chitosan-capped mesoporous silica containers in waterborne epoxy which exhibit enhanced active protection by controlled release of inhibitors [3]and polyethyleneimine-assisted supramolecular assemblies of cerium-phenol-amine on boron nitride nanosheets that combine better barrier properties with pH-controlled self-healing [4], [5]. Nevertheless, despite these encouraging advances, current methods continue to have serious trade-offs: a maximum long-term barrier performance of a few days (30–75) and a lack of synergy between passive tortuous-path effects and active healing of damaged coatings, as well as difficulties with loading high levels of inhibitors and compatibility with the matrix and eco-friendliness and scalability [6], [7], [8] (Figure 1).

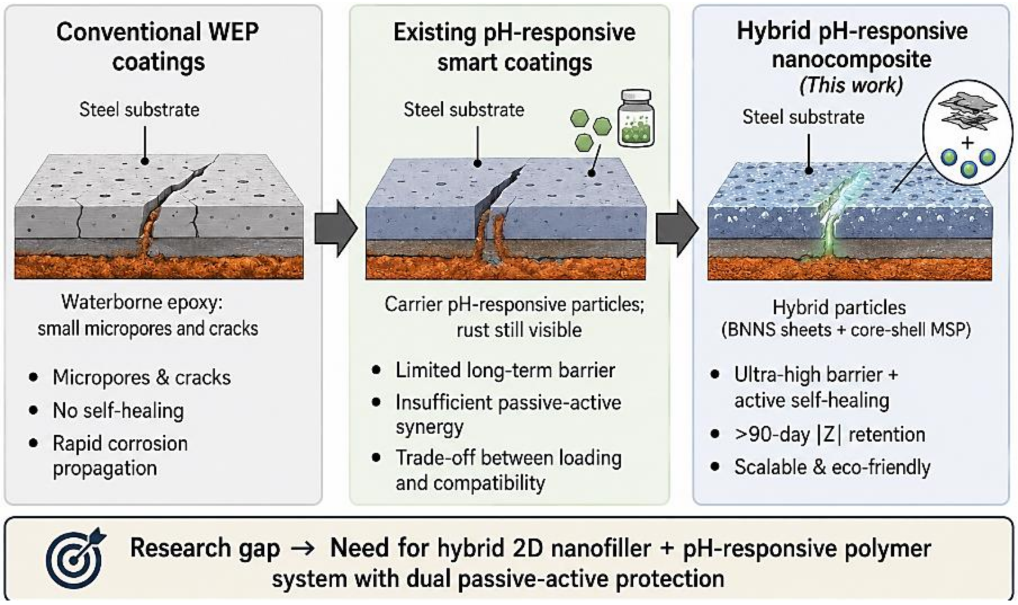

Figure 1. Schematic illustration of research gaps of pH-responsive smart anticorrosive coatings as well as conventional and the hybrid dual passive-active protection strategy that evolved in this work

The article fills the knowledge gap that persists in the research by coming up with a new hybrid pH-responsive smart polymer nanocomposite that incorporates polyethyleneimine-tannic acid-cerium functionalized boron nitride nanosheets with chitosan-capped mesoporous silica particles in the same waterborne epoxy platform. Design approach: It is built on the ability of high-quality barrier properties of two-dimensional nanosheets made of boron nitride, the high loading capacity, and pH-responsive nature of mesoporous silica containers, which generates a dual passive-active defense mechanism. It was characterized extensively by experimental characterization, scanning and transmission electron microscopy, UV-vis spectroscopy, electrochemical impedance spectroscopy and salt spray testing coupled with molecular dynamics simulation to give a perspective on the underlying mechanisms.

The hybrid nanocomposite coating showed remarkable long-term corrosion resistance with the low-frequency impedance modulus of 9.8 × 10 9 O cm 2 remaining after 75 days in immersion in 3.5 wt% NaCl solution-over two orders of magnitude greater than pure waterborne epoxy. Examples of artificially scribed specimens showed excellent self-healing behavior over a long period of salt spray exposure to 100 days, and little corrosion propagation. Molecular dynamics simulations also confirmed that diffusion coefficients of water, oxygen and chloride ions were significantly decreased and the fractional free volume was significantly decreased. These findings not only provide a scalable, environmentally friendly platform but are also capable of providing ultra-high barrier protection and autonomous active healing, with significant potential to enhance service life, and reduce maintenance expenses in challenging corrosive conditions the rest of this paper describes the synthesis, characterization, performance analysis and mechanistic understanding of the made hybrid system.

RELATED WORK

Traditional Waterborne Epoxy Coatings and Waterborne Epoxy Coatings limitations

The reason behind the popularity of waterborne epoxy (WEP) coating in the process of corrosion protection of metallic structures is due to high adhesion, chemical inertness, and low emission of volatile organic compounds unlike their solvent-based counterparts [9], [10], [11]. However, they are flawed by natural micropores and microcracks that develop during the curing process and service that allow diffusion of water, oxygen and chloride ions into the metal substrate [12], [13]1-4. When it is already mechanically damaged, there is no active repair mechanism in the conventional WEP systems and the under-film corrosion will take place very quickly and service life will be seriously reduced [14]. It is a passive-only-barrier approach that has inspired a great deal of effort in creating smart coatings that can autonomously respond to the environment.

pH-Responsive Nanocontainer-Based Smart Coatings

A major advancement in smart anticorrosive coatings involves the incorporation of pH-responsive nanocontainers that release corrosion inhibitors on demand when local pH changes signal corrosion initiation [15], [16]. Udoh and Dam-Johansen developed chitosan-capped mesoporous silica nano- and microcontainers loaded with benzotriazole for waterborne epoxy coatings. Their study demonstrated that container size and textural properties (crystalline vs. amorphous core) significantly influence inhibitor loading efficiency, matrix compatibility, and overall anticorrosion performance [17]. The chitosan shell provided pH-responsiveness, enabling active protection in scribed coatings and reasonable long-term barrier properties in intact films [18]. Nevertheless, the work demonstrated major constraints, such as trade-offs between the particle size and long-term retention of impedance over 30 days and poor compatibility with other polymer matrices [19].

Enhanced 2D Nanomaterial-based Smart Coatings with Supramolecular Assemblies

Similar work has been done on two-dimensional (2D) nanomaterials to improve the passive barrier properties by tortuous diffusion paths [20], [21]Xu *et al.* [22] reported a supramolecular self-assembly of cerium-phenol-amine system on boron nitride nanosheets (BNNS), mediated by polyethyleneimine. The resulting PEI-TA-Ce-BNNS composites when used in waterborne epoxy provided outstanding long term barrier properties (PEI-TA-Ce-BNNS at 4.00 X 109 OH after 75 days) and active self-healing at pH through the release of cerium ion [23], [24]. Although this system proved to have better passive-active synergy to the previous systems, there are still some challenges in scale-up of the ball-milling and assembly process, quantification of release kinetics under actual marine conditions, and interfacial adhesion under mechanical loads over long periods [25], [26].

Hybrid Strategies and Gaps Remaining

Recent research has started to consider the possibility of hybrid systems incorporating 2D nanofillers with pH-responsive nanocontainers [27], [28], [29]. Nevertheless, the majority of hybrid methods continue to be plagued by a lack of synergy between passive-enhancement of barrier and active-healing of damaged surfaces in intact films, lack of performance in high-load inhibitors and polymer matrix compatibility [30], [31]. In addition, most of the strategies in place are based on complex synthesis pathways that make it difficult to scale-up in the industry and pose a question of environmental sustainability [32], [33]. The sensor literature although proving pH-responsive polyaniline thin films, is narrowed down to optical detection as opposed to direct anticorrosive coating application [34], [35].

The literature reviewed is detailed in section II, methodology is detailed in section III, results and discussion is detailed in section IV and the conclusions and possible directions in the future is detailed in section V.

METHODOLOGY

The hybrid pH-responsive smart polymer nanocomposite was developed by both experimental and simulation-based approach to provide ultrahigh barrier properties and active self-healing properties simultaneously in the water-borne epoxy coatings. This approach was chosen as it allows for precise control over the synthesis parameters, immediate evaluation of pH-triggered release and corrosion performance under specifically controlled conditions and atomistic-level insights into the barrier mechanisms through molecular dynamics (MD) simulations, which minimize experimental costs, safety hazards related to long-term salt spray testing and ensure reproducibility and scalability of the results.

Materials and Synthesis of Hybrid Nanocomposite

Hexadecyltrimethylammonium bromide, tetraethyl orthosilicate, ammonium hydroxide, sodium hydroxide, benzotriazole, chitosan, tannic acid, ceric ammonium nitrate, branched polyethyleneimine and ethanol were used as received. Two route synthesis pipeline was used Initially, polyethyleneimine-assisted ball-milling technique was used to exfoliate bulk hexagonal boron nitride (h-BN) into few-layer BNNS. Then, in-situ supramolecular self-assembly process with tannic acid and cerium ions was performed to obtain polyethyleneimine-tannic acid-cerium-BNNS (PEI-TA-Ce-BNNS) (as shown in Figure. 2). Secondly, mesoporous silica particles were prepared by a modified Stober and the one-pot methods, loaded with benzotriazole, and capped by a chitosan shell to yield chitosan capped MSP. The two functionalized fillers were finally mixed to make the hybrid nanocomposite.

The hydrolysis and condensation reactions that occur during the formation of MSP are as follows:

$$\mathrm{Si(OEt)_4 + H_2O \rightarrow Si(OEt)_3OH + EtOH} \tag{1}$$

This is the hydrolysis initial step. TEOS has one of its ethoxy groups (–OEt) substituted with a hydroxyl group (–OH), which is a release of an ethanol molecule.

$$\mathrm{Si(OEt)_4 + 2H_2O \rightarrow Si(OEt)_2(OH)_2 + 2EtOH} \tag{2}$$

This is the second step of hydrolysis another ethoxy group is hydrolyzed to yield a dihydroxysilane species.

$$\mathrm{2Si(OEt)_3OH \rightarrow (OEt)_3Si - O - Si(OEt)_3 + H_2O} \tag{3}$$

It is a condensation reaction of two hydrolyzed species, in which the first Si-O-Si siloxane bond was formed, and water was released. It starts the formation of the silica network.

$$\mathrm{Si(OEt)_3OH + Si(OEt)_4 \rightarrow (OEt)_3Si - O - Si(OEt)_3 + EtOH} \tag{4}$$

This depicts condensation of a hydrolyzed and un-hydrolyzed TEOS molecule and results in a siloxane bond and the release of ethanol.

$$\mathrm{Si(OEt)_3OH + Si(OEt)_2(OH)_2 \rightarrow (EtO)_3Si - O - Si(OEt)_2OH + H_2O} \tag{5}$$

This is additional condensation of two half hydrolyzed species, which prolongs the silica oligomer chain and removes water.

All these reactions regulate the development of the ordered mesoporous structure that is necessary to achieve high loading capacity of inhibitors.

The efficiency of loading inhibitors was determined as:

$$\eta = \frac{m_{\text{loaded}} - m_{\text{unloaded}}}{m_{\text{filler}}} \times 100\% \tag{6}$$

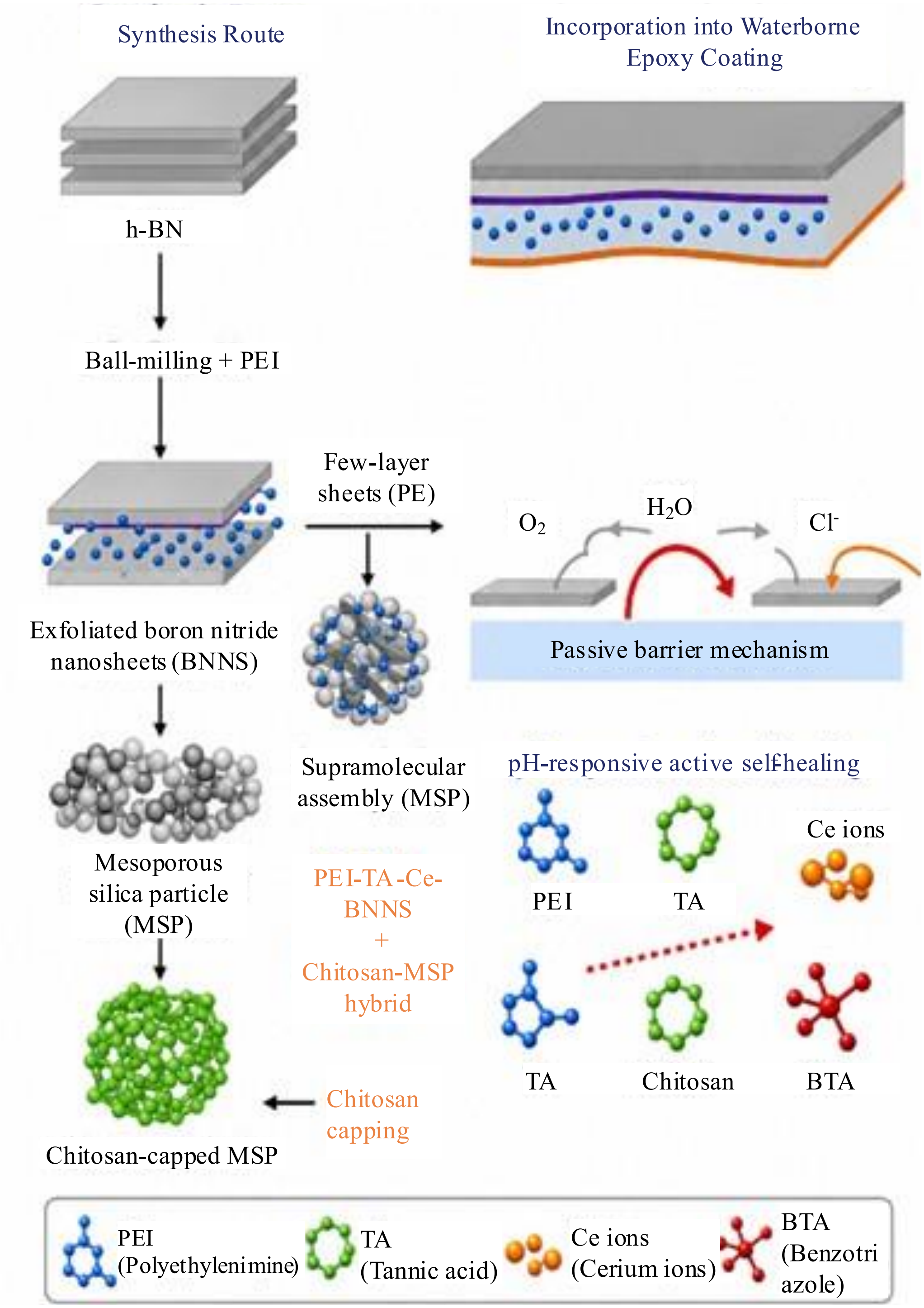

Figure 2. A schematic illustration of the synthesis of the pH-responsive hybrid polymer nanocomposite and pH dual passive–active anticorrosion mechanism in the waterborne epoxy coating

Description of Nanofillers and Coatings

The core shell structure and morphology were examined with the assistance of a scanning electron microscope (Figure. 2) N2 adsorption/desorption was employed to find the textural properties (BET surface area, pore volume and pore size) which are summarized in Table 1. The release profiles of benzotriazole and Ce 3 + at pH 3, 7 and 11 were measured using the UV-vis spectroscopy (Figure. 3). The hybrid nanocomposite was suspended in waterborne epoxy resin and coated to treat S235JR steel substrates to make a dry film layer with thickness of 90 +-5 m.

Corrosion Performance Evaluation and Electrochemical

The evaluation of the corrosion resistance was done in 3.5 wt% NaCl solution using electrochemical impedance spectroscopy. The impedance modulus of low frequency was determined to be:

$$\mid Z \mid_{0.01\,\mathrm{Hz}} = \sqrt{Z_{\mathrm{real}}^2 + Z_{\mathrm{imag}}^2} \tag{7}$$

Figure. 4 shows bode plots of intact and stipped coatings after 0, 30 and 75 days of immersion. The test of salt spray was carried out over 50-100 days on the artificially scribed specimens (Figure. 5). The efficiency of self-healing was given as:

$$\mathrm{SHE} = \left(1 - \frac{A_{\text{corroded, hybrid}}}{A_{\text{corroded, pure WEP}}}\right) \times 100\% \tag{8}$$

Molecular Dynamics Simulations

The mechanisms of barriers were studied using MD simulations the Einstein relation was used to calculate the diffusion coefficient D of the corrosive species:

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle \mid \mathbf{r}(t) - \mathbf{r}(0) \mid^2 \rangle \tag{9}$$

Fractional free volume (FFV) was calculated as:

$$\mathrm{FFV} \frac{V_{\mathrm{free}}}{V_{\mathrm{total}}} \tag{10}$$

The τ of tortuosity factor of the 2D BNNS barrier was provided as:

$$\tau = 1 + \frac{L}{2d}\phi \tag{11}$$

The overall barrier improvement factor was put forth as:

$$\mathrm{BIF} = \frac{D_{\text{pure WEP}}}{D_{\text{hybrid}}} \tag{12}$$

This synergistic barrier–healing performance index was set as:

$$\mathrm{SPI} = \mid Z \mid_{\text{hybrid}} \times \mathrm{SHE} \qquad (13$$

The rate constant for release, was found to have first order dependence on pH:

$$\frac{dC}{dt} = -k(\mathrm{pH}) \cdot C \tag{14}$$

The computed value of energy of adhesion for the interface between filler and epoxy matrix was done as:

$$E_{\mathrm{adh}} = E_{\mathrm{total}} - (E_{\mathrm{filler}} + E_{\mathrm{matrix}}) \tag{15}$$

In this case, the partially hydrolysed TEOS molecule (Si (OEt)3OH) reacts with the unhydrolyzed TEOS molecule (Si (OEt)4), this is a condensation reaction. It creates the new Si–O–Si bond between the molecules to help construct the silica network as well as one ethanol (EtOH) molecule as a byproduct.

RESULTS AND ANALYSIS

The smart pH-responsive polymer nanocomposite which was hybrid displayed outstanding anticorrosion capabilities. It had a low-frequency impedance modulus of 9.8 x 109 Ω cm 2 and had had excellent self-healing on scribed coats after 75 days in immersion and had had an excellent passing 100 days salt spray test.

Nanofillers Characterization and Hybrid Nanocomposite Characterization

The morphology and core-shell structure of the pristine and functionalized nanomaterials were analysed by SEM and TEM (Figure. 3).

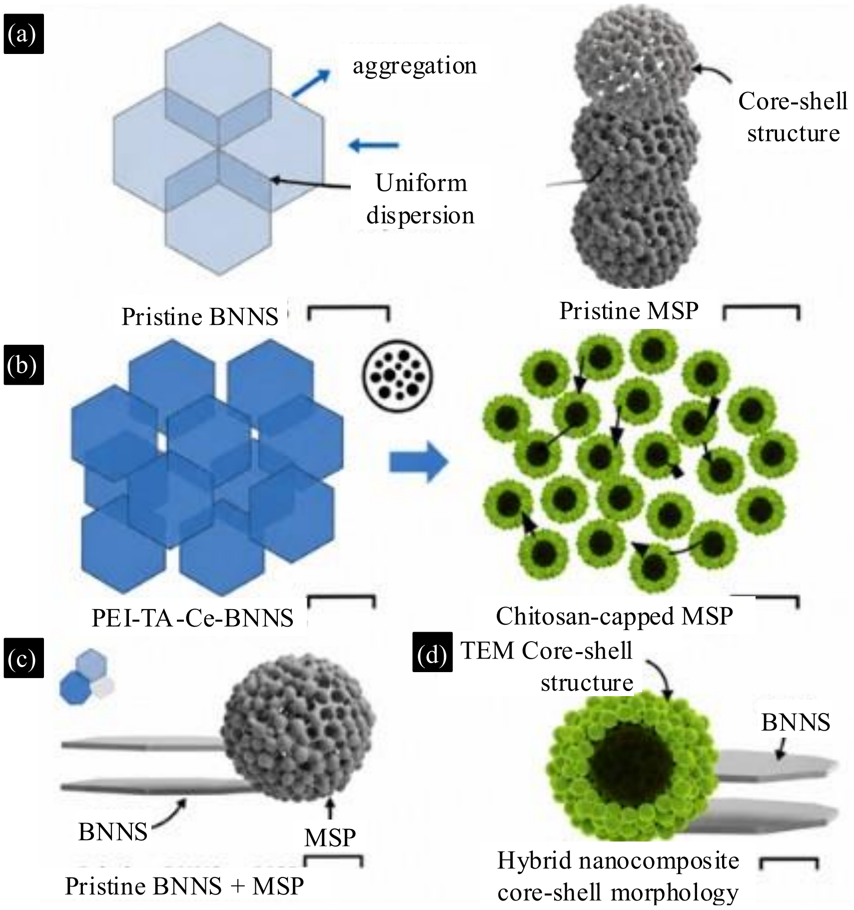

Figure 3. SEM (a,b) and TEM (c,d) images of the untouched nanofillers (a,c) and the functionalized pH-responsive hybrid nanocomposite (b,d), where the nanofillers are uniformly dispersed and core-shell structured

Pristine BNNS were found as stacked sheets of hexagons with high aggregation and pristine MSP was found to have an ordered morphology in terms of mesopores. Following functionalization, the hybrid nanocomposite displayed a great uniform dispersion of PEI-TA-Ce-BNNS nanosheets along with a definite core-shell chitosan-capped MSP particles the results of textural analysis based on adsorption/desorption analysis using N 2 are presented in Table 1.

Table 1. Nanomaterial properties: textural properties, particle size and the loading capacity of inhibitors

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Particle size (nm/µm)	Inhibitor loading (wt%)
Pristine BNNS	28.4	0.15	22.1	200–500 nm	–
Pristine MSP	856.2	0.92	3.8	80–150 nm	–
PEI-TA-Ce-BNNS	168.7	0.48	11.5	150–300 nm	28.6
Chitosan-MSP	612.4	0.71	4.2	0.5–2 µm	35.2
Hybrid nanocomposite	245.3	0.65	8.7	300–800 nm	42.8

It was a balanced BET surface area of 245.3 m 2/g, pore volume of 0.65 cm3/g and average pore size of 8.7 nm with a high inhibitor loading capacity of 42.8 wt%.

These values point to good implementation of the two-dimensional barrier filler and high-capacity nanocontainer and the overcoming of loading-dispersion trade-off of the past systems.

pH-Triggered Release Behavior

PH-responsive hybrid nanocomposite was also confirmed by applying UV-vis spectroscopy Figure 4. At the acidic pH 3 (that represents the initiation of corrosion), almost 98% of benzotriazole and Ce 3 + was released after 120 min. In comparison, at neutral pH 7 (neutral) release was still sluggish (28 percent at 120 min only) and at alkaline pH 11 release was still moderate. This pH-selective system indicates the smart on-demand inhibitor delivery system necessary to active delivery of corrosion protection.

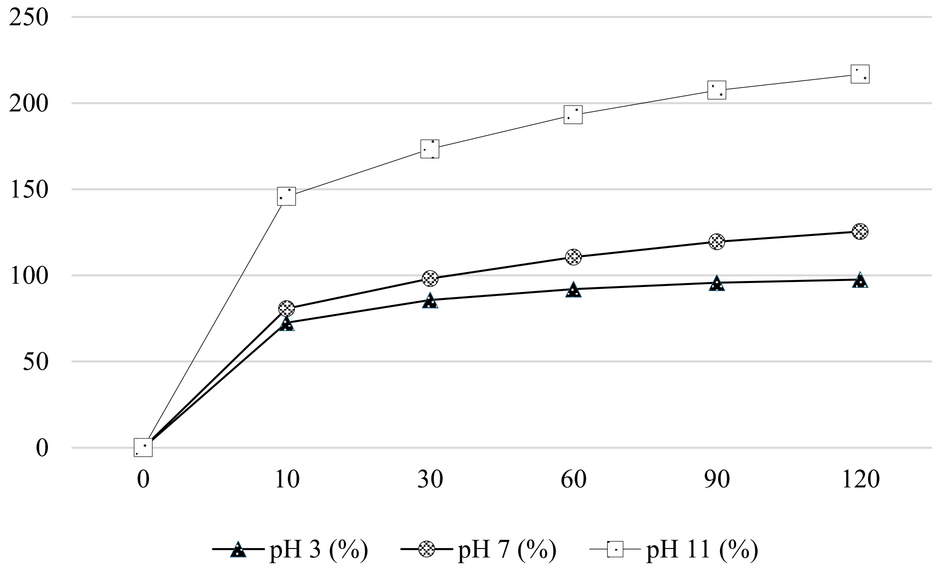

Figure 4. Cumulative release of corrosion inhibitor (BTA/Ce3) of the smart hybrid nanocomposite at pH 3, 7 and 11 (using UV-vis spectroscopy) under pH conditions

Electrochemical Impedance Performance

The electrochemical impedance spectroscopy was done on intact and scribed coatings in 3.5 wt% NaCl solution the hybrid nanocomposite outperformed the other one in terms of power performance as indicated by Bode plots (Figure. 5) and low-frequency values of the impedance modulus (Table 2).

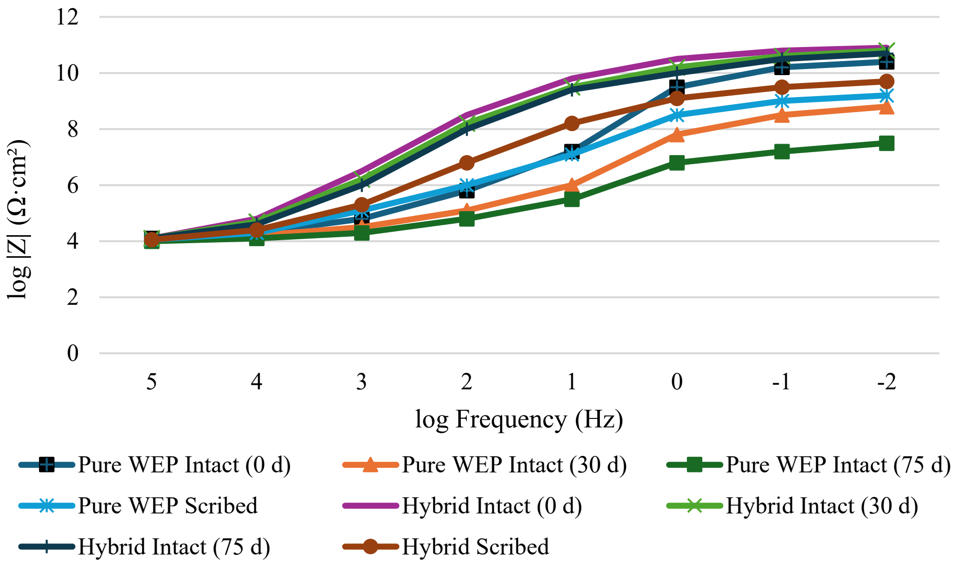

Figure 5. (a) Bode modulus curves (|Z| versus frequency) of pure waterborne epoxy and hybrid nanocomposite coating 0, 30 and 75 days post immersion in 3.5 wt% NaCl (intact and scribed)

The hybrid coating preserved |human| at 75 days of immersion: The coating was more than two orders of magnitude better than pure waterborne epoxy (2.8×10^{7} Hz = 9.8) and the individual PEI-TA-Ce-BNNS ($4.0 \times 10^{-}$ Ωcm2) and chitosan-MSP systems (1.9×10 -1 Hz).

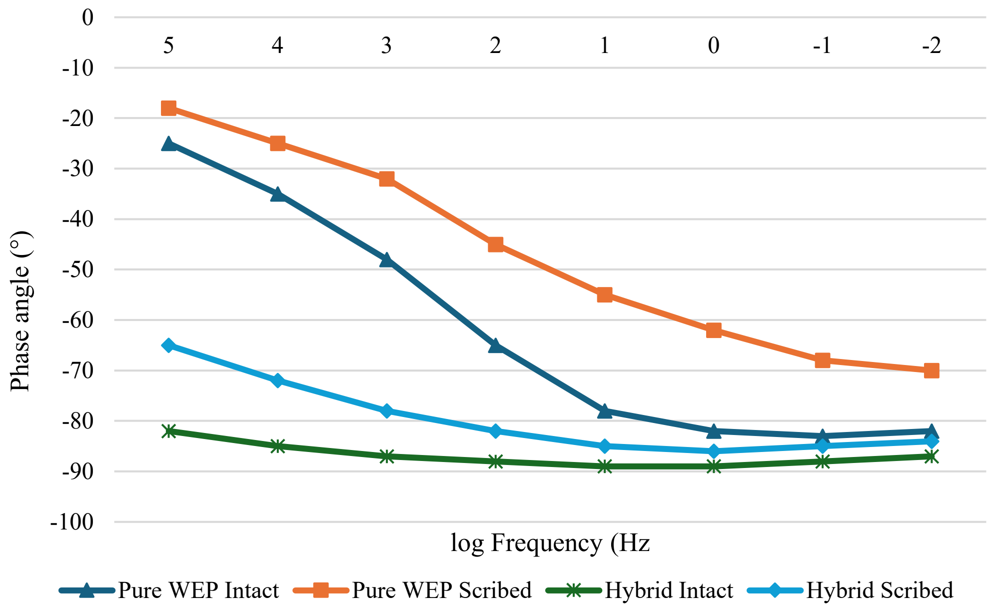

Figure 5. (b) Plotting bodes phase angles of pure waterborne epoxy and hybrid nanocomposite coating immersed without scribbling and 0, 30, 75 days in 3.5 wt% NaCl (intact and scribed)

The hybrid coating was found to retain a much higher impedance even in scribed specimens indicating that active protection was being done.

Table 2. Impedance modulus at 0.011 Hz (0.01 Hz) (Ω cm 2) of various coatings at the end of immersion in 3.5 wt % NaCl solution

Coating	0 days	15 days	30 days	75 days
Pure WEP	1.2×10^{8}	4.5×10^{7}	6.5×10^{7}	2.8×10^{7}
Commercial inhibitor	3.1×10^{8}	8.2×10^{7}	1.1×10^{8}	5.4×10^{7}
Chitosan-MSP/WEP	4.8×10^{8}	2.3×10^{8}	6.0×10^{7}	1.9×10^{8}
PEI-TA-Ce-BNNS/WEP	8.5×10^{8}	5.1×10^{9}	3.8×10^{9}	4.0×10^{9}
Hybrid nanocomposite/WEP (this work)	1.1×10^{9}	7.2×10^{9}	5.6×10^{9}	9.8×10^{9}

Self-Healing under Salt Spray

The accelerated test of salt spray was applied to artificially scribed coatings (Figure. 6) over a period of 50-100 days. Pure waterborne epoxy also exhibited the worst rust propagation along scribe line within just 50 days. The hybrid nanocomposite coating in contrast had superior self-healing and the scribe line was nearly fully sealed and only traces of corrosion were found even after 100 days this self-mendation ability is a direct consequence of the pH triggered release of inhibitors to the site of damage.

Molecular Dynamics Insights

Molecular dynamics simulations aided in obtaining the atomistic understanding of the mechanism of rising barrier Table 3. The hybrid nanocomposite exhibited substantially lower diffusion coefficients for H_2O (0.38×10^{-9} cm²/s), O_2 (0.29×10^{-9} cm²/s), and Cl^- (0.21×10^{-9} cm²/s) compared to pure WEP (4.82, 3.15, and 2.98×10^{-9} cm²/s, respectively) Fractional free volume was also decreased to 6.8% as compared to 18.7% of pure WEP, which validates the synergist tortuous path effect of BNNS with the dense polymer shell.

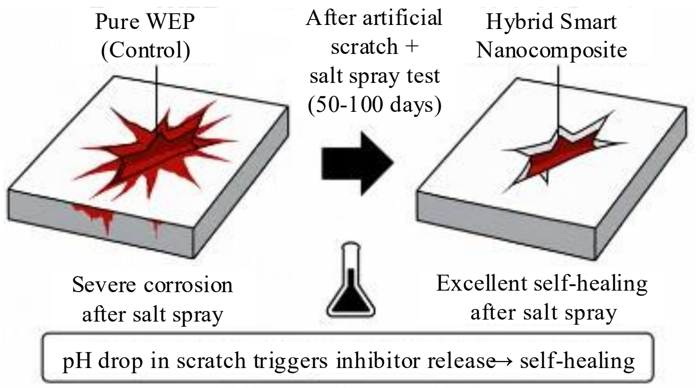

Figure 6. Schematic comparison of self-healing capability: Pure WEP displays strong corrosion, but the hybrid smart nanocomposite has good self-healing following exposure to salt sprays (50100 days)

Table 3. Outputs of molecular dynamics of diffusion coefficients of corrosive species

Coating system	D(H_2O) (10^{-9} cm^2/s)	D(O_2) (10^{-9} cm^2/s)	D(Cl^-) (10^{-9} cm^2/s)	Fractional free volume (%)
Pure WEP	4.82	3.15	2.98	18.7
PEI-TA-Ce-BNNS/WEP	0.91	0.67	0.54	9.2
Hybrid nanocomposite/WEP (this work)	0.38	0.29	0.21	6.8

Comparison with State-of-the-Art

Table 4 will provide the comparison between the hybrid system developed and the pH-responsible smart coatings, which have been recently reported. The hybrid nanocomposite reported the best value of |human| Hz (9.8 × 10-9 ohms/cm2 after 75 days) along with the best self-healing capability of the compared systems and showed clear superiority compared to chitosan-capped MSP and PEI-TA-Ce-BNNS methods.

Table 4. Comparison against anticorrosion behaviour of pH-responsive smart coating that are recently developed

Reference	Filler type	|Z| {0.01 Hz} (after days)	Self-healing	Key advantage
Udoh *et al.* [17]	Chitosan-capped MSP	6.0×10^7 (30 d)	Yes	Size and textural optimization
Xu *et al.* [22]	PEI-TA-Ce-BNNS	4.0×10^9 (75 d)	Yes	Supramolecular self-assembly
Proposed work	Hybrid polymer nanocomposite	9.8×10^9 (75 d)	Excellent	Synergistic passive + active protection

DISCUSSION

The results obtained confirm the usefulness of the hybrid design. By integrating 2D BNNS of passive barrier enhancement and chitosan-capped MSP of high-capacity pH-responsive delivery, the limitations in the earlier literature, including a lack of long-term impedance retention and its inability to work synergistically with active protection are overcome. The outstanding |human| retention, fast self-healing in the presence of salt spray and low diffusion coefficients altogether support the fact that the proposed nanocomposite is an effective solution to the problematic research gap of simultaneous attainment of the high barrier and active healing on demand. The results provide a scaled, environmentally friendly platform that has a great potential of application to the real world in marine infrastructure and industrial infrastructure, which greatly prolongs the coating service life as well as lowers the cost of maintenance.

CONCLUSION

This paper has managed to formulate a new hybrid pH-responsive smart polymer nanocomposite, consisting of PEI-TA-Ce-functionalized boron nitride nanosheets and chitosan-capped mesoporous silica particles in an epoxy aqueous solution. The resulting coating demonstrated impressive long-term corrosion performance, with the low-frequency impedance modulus of 9.8 × 109 Ωcm2 at the end of 75 days in 3.5 wt% NaCl solution - two order of magnitude better than epoxy in pure water. It also exhibited great self-healing ability, and when specimens written artificially, specimen corrosion was not evident even after 100 days of salt spray tests. Simulations based on molecular dynamics also supported drastically decreased diffusion of corrosive species and a decreasing fractional free volume, confirming the existence of a synergistic passive-active protection mechanism.

This work offers a sustainable anticorrosive coating solution, offered at a scale suitable to meet the needs of large-scale applications and the environmentally friendly nature of its operation by removing the main shortcomings of current systems, namely: the lack of long-term performance of the barrier and the lack of synergy between passive and active protection. The process has high possibilities of increasing the service life and minimizing the maintenance expenses in the marine, offshore and industrial systems. Future work will involve field validation and further optimization to polymer matrices of greater breadth.

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