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Research Progress on the Application of Graphene-Modified Anti-Corrosion Coatings

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ABSTRACT
The splash zone in marine environments represents the area of most severe corrosion for steel facilities. Although traditional anti-corrosion coatings offer excellent performance, they often fail to provide long-term effective protection. Current research focuses on incorporating reinforcing phases during preparation to enhance coating properties. Compared to traditional reinforcements like metallic zinc powder, micaceous iron oxide, or fibers, graphene, with its two-dimensional lamellar structure, can significantly improve the anti-corrosion capacity of coatings. This paper reviews common preparation methods for graphene-modified anti-corrosion coatings, details the performance of such coatings in terms of salt spray resistance and chemical corrosion resistance, and discusses factors hindering performance enhancement, such as dispersion homogeneity and disordered random arrangement. The severity of marine corrosion and the importance of developing various anti-corrosion technologies are emphasized.

KEYWORDS
Graphene; Anti-corrosion coatings; Marine corrosion; Preparation methods; Modification

1 Introduction

With the aggravation of atmospheric pollution, cross-sea bridges in coastal marine atmospheric corrosion zones are subjected to high humidity and high salinity environments. Chloride ions in salt spray, characterized by strong permeability and high corrosivity, make it difficult for various steel and reinforced concrete structures to maintain a passive state, rendering them highly susceptible to electrochemical corrosion While traditional anti-corrosion coatings meet these requirements to some extent, the corrosion failure and peeling of zinc coatings on critical parts of steel facilities are becoming increasingly severe. This corrosion not only erodes the metal structure, gradually reducing its strength, but also accelerates the aging process. Catastrophic corrosion can lead to severe damage and significant economic losses. Graphene, owing to its unique electrical conductivity, high adsorption capacity, and mechanical properties, has been introduced into the realm of heavy-duty anti-corrosion coatings. Its incorporation enhances the protective performance of coatings and offers new possibilities for developments in offshore oil and gas field development, port construction, cross-sea bridges, subsea tunnels, ship engineering, and deep-sea exploration in China.

2 Properties of graphene

Graphene is a two-dimensional material consisting of carbon atoms arranged in a hexagonal honeycomb lattice via sp^2 hybrid orbitals, exhibiting exceptional properties such as extreme thinness (single carbon atom thickness), high strength, high electrical and thermal conductivity [2]. It serves as the fundamental building block for other graphitic materials (like fullerenes, carbon nanotubes, and graphite). With a thickness of merely one atomic layer (approx. 0.335 nm), graphene is the thinnest known 2D material. Incorporating graphene as a nanofiller into protective coatings is one of the most common strategies for enhancing their performance. The improvement in anti-corrosion properties primarily stems from two aspects: firstly, graphene effectively fills micropores and microcracks formed during coating curing, enhancing coating densification; secondly, its two-dimensional layered structure provides an excellent physical barrier effect against corrosive media.

2.1 Barrier effect

In the graphene structure, the C---C bond length is 0.142 nm, and the van der Waals radius of a carbon atom is approximately 0.11 nm, resulting in a regular hexagonal pore size of only 0.064 nm. Due to this nanoscale pore structure, graphene exhibits superior barrier properties against corrosive species (such as H_2O, O_2, Cl^-), enabling efficient physical shielding within anti-corrosion coatings. Scanning Electron Microscopy (SEM) observations indicate that before neutral salt spray testing, the surface of graphene-zinc powder coatings is significantly denser, whereas traditional zinc-rich primers exhibit a visibly porous structure. Furthermore, as a two-dimensional nanomaterial, graphene can effectively fill microvoids and gaps within the coating, further increasing its density. Figure 1 shows a Transmission Electron Microscopy

(TEM) image of a composite coating, clearly displaying the typical two-dimensional thin-layer morphology of graphene, providing direct evidence for its distribution and mechanism of action within the coating.

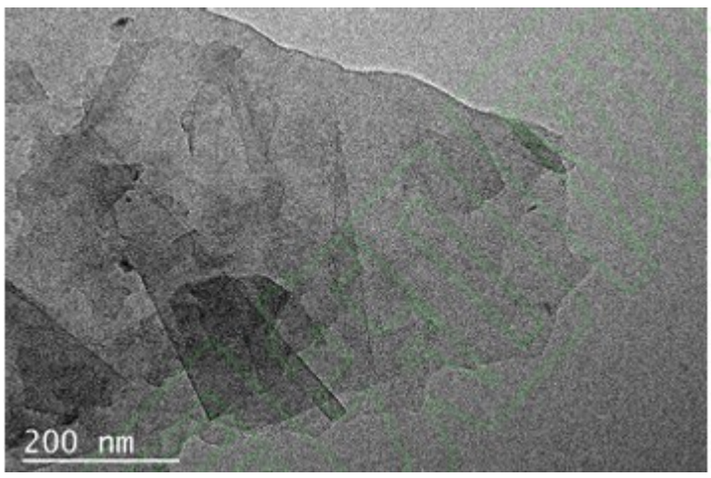

Figure 1 TEM image of graphene.

2.2 Labyrinth effect

Graphene, as a novel nano-sheet material, significantly enhances the physical barrier properties of anti-corrosion coatings due to its high specific surface area, nanoscale thickness, and two-dimensional flake structure. Its closely packed hexagonal lattice composed of sp^2 hybridized carbon atoms possesses high electron cloud density, demonstrating remarkable molecular impermeability. Within the coating, graphene can form highly tortuous diffusion pathways, delaying the penetration of corrosive media, a phenomenon known as the "labyrinth effect". Simultaneously, its uniform dispersion helps improve coating density, reduce porosity, and thus enhance the protective capability for the metal substrate. Consequently, graphene is widely used to modify polymer matrices to improve the comprehensive performance of anti-corrosion coatings.

2.3 Synergistic cathodic protection

To enhance the protective performance for metal substrates, traditional anti-corrosion coatings for metal surfaces often contain a high proportion of functional fillers like zinc or aluminum powder. When corrosion initiates in the coating system, the zinc or aluminum powder acts as a sacrificial anode, corroding preferentially to protect the metal substrate functioning as the cathode.

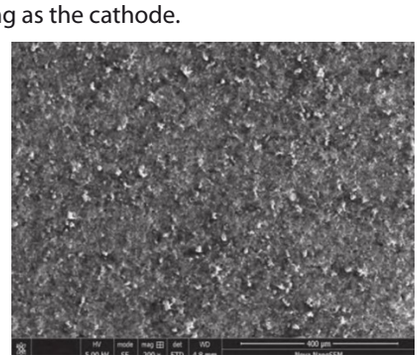

Figure 2 Graphene-zinc powder coating

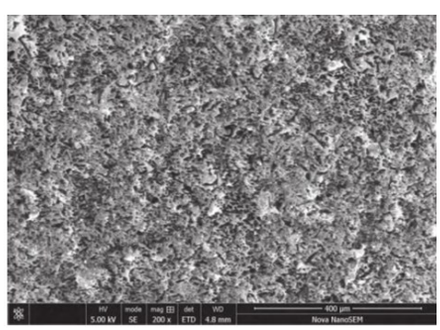

Figure 3 Zinc-rich primer

Comparison of Figure 2 and Figure 3 reveals that the surface of the graphene-zinc powder coating is much less porous and significantly denser than that of the zinc-rich primer. In epoxy zinc-rich primers, only 25% to 30% of the total zinc powder actually participates in the cathodic protection reaction as the anode; the majority of the remaining zinc powder primarily serves as a conductive medium. Highly conductive graphene can significantly enhance the electrochemical connection between zinc particles and the steel substrate, increase the activation utilization rate of zinc powder, thereby reducing the effective amount of zinc powder required and extending the duration of cathodic protection provided by the coating.

3 Graphene anti-corrosion films and coatings

As a novel protective material, graphene anti-corrosion coatings are mainly divided into two categories: pure graphene film coatings and graphene composite coatings. The performance of pure graphene film coatings highly depends on electrodeposition process parameters and the chemical composition of the graphene precursor. Their composition and protection mechanisms are relatively singular, and production costs are high. These factors impose significant limitations on their application in large-scale marine steel structure anti-corrosion projects, making it difficult to meet the demands of harsh marine corrosive environments. In contrast, graphene composite coatings, by combining with other functional materials, not only have relatively simpler preparation processes but also effectively overcome the shortcomings of single-component graphene coatings, significantly improving their overall protective performance. Such coatings exhibit good long-term protective efficacy and are more suitable for the current corrosion protection requirements of marine steel structures.

4 Research progress on properties of graphene-modified anti-corrosion coatings

4.1 Preparation methods for graphene-modified anti-corrosion coatings

4.1.1 Melt blending method

Melt Blending is a widely used physical mixing process in the field of polymer materials. Its basic principle involves using thermal energy and mechanical shear to mix two or more polymers (or polymers with additives/fillers) in a molten state to achieve uniform dispersion of components, improve material properties, or impart new material properties. When preparing graphene-modified anti-corrosion coatings, the polymer matrix components are first heated above their melting point or viscous flow temperature to convert them into a viscous melt. Subsequently, uniform polymer melt is prepared using mixing equipment like internal mixers or extruders. Graphene or its derivative fillers are then added to the melt and effectively dispersed through intense shear. Finally, the graphene/polymer composite is obtained upon cooling and solidification.

4.1.2 Solution blending method

Solution Blending is a technique for preparing composite materials by co-dissolving different polymers or functional materials in a solvent to form a homogeneous solution, followed by solvent removal. This method enables uniform dispersion at the molecular level and is one of the key techniques for preparing polymer blends, nanocomposites, and functional films. In the preparation of graphene-based composites, graphene or its derivatives are first uniformly dispersed in a solvent to obtain a stable graphene dispersion. The organic polymer is then gradually dispersed into this solution. Thorough mixing and dispersion are achieved through mechanical stirring, ball milling, or shear emulsification. Finally, the solvent is removed (and polymer polymerization may be initiated) via a heating/curing process, resulting in graphene dispersed within the polymer matrix.

4.1.3 In situ polymerization method

In situ polymerization is an important material preparation technology whose core principle involves introducing monomers (or prepolymers) into the interior or interface of a specific substrate and directly initiating polymerization within this confined space to form the polymer phase. Distinguished from traditional "blending methods", this approach, by constructing the polymer phase directly at the target location, can significantly improve the compatibility, dispersibility, and interfacial interactions between the polymer and the substrate. This method typically involves blending polymerizable monomers (or microemulsion prepolymers) with graphene or its derivatives, adding an appropriate initiator, and then initiating in situ polymerization of the monomers by controlling parameters such as temperature and reaction time, thereby achieving uniform dispersion of graphene within the polymer matrix.

4.1.4 Organic small molecule modified graphene anti-corrosion coatings

Introducing aminosilane coupling agents can effectively enhance the interfacial interaction between graphene and polymer emulsions, significantly improving their compatibility. By adjusting the amphiphilicity and interlayer spacing of graphene, its dispersion behavior within the polymer matrix can be further optimized, providing an effective pathway for achieving more uniform covalent modification of graphene.

The surface of graphene oxide (GO) is rich in oxygen-containing functional groups, providing abundant reactive sites for amino modification. Utilizing condensation reactions between amino modifiers and carboxyl groups on the GO

surface, as well as ring-opening reactions with epoxy groups, amino functional groups can be successfully grafted onto the GO surface, forming stable covalent bonds. This chemical modification improves the dispersibility of GO in epoxy resin coatings; the synergistic effect of condensation and ring-opening reactions ensures uniform distribution of modified GO within the epoxy resin matrix, subsequently forming a denser protective layer and significantly improving the interfacial compatibility between GO and the epoxy resin [2].

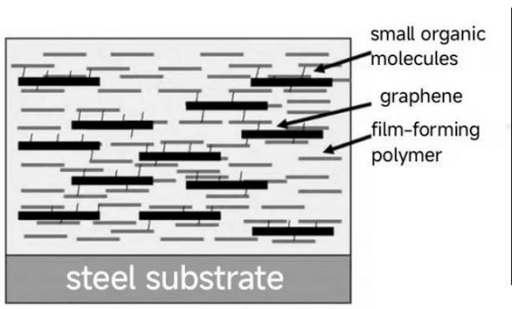

Figure 4 Schematic diagram of the anti-corrosion mechanism of organic small molecule modified graphene anti-corrosion coatings [2]

In 2023, Huang Zhixiong's research group [2] modified graphene with sodium 2, 2'-methylenebis(4, 6-di-tert-butylphenol) phosphate (NA-11) to enhance its dispersibility and compatibility in water-based epoxy resin, successfully preparing composite coatings with excellent anti-corrosion properties. The results showed that NA-11 modified graphene significantly improved the coating's corrosion protection effectiveness. The protective mechanism originates from the inherent physical barrier effect and "labyrinth effect" of graphene, combined with the efficient corrosion inhibition effect of NA-11, collectively strengthening the long-term protective capability of the coating for the metal substrate.

4.2 Physicochemical properties of graphene-modified anti-corrosion coatings

In major projects such as marine oil and gas development, port construction, and offshore wind power in China, various types of steel structures and reinforced concrete facilities are widely used. Their service environments are becoming increasingly diverse and extreme, posing severe challenges to the performance of graphene-modified anti-corrosion coatings. According to corrosion characteristics, the marine environment can be divided into typical zones such as the atmospheric zone, the splash zone, and the full immersion zone in seawater [6]: The atmospheric zone is characterized by high humidity, high chloride ion content, and significant dry-wet alternation; The splash zone has sufficient oxygen supply and is affected by the synergistic effect of multiple environmental factors, resulting in the most severe corrosion; The full immersion zone is prone to the formation of oxygen concentration difference cells due to uneven attachments, which accelerates local corrosion. Under such harsh conditions, the comprehensive performance of graphene-modified anti-corrosion coatings directly affects the reliability and service life of equipment. Specifically, their mechanical properties ensure the wear resistance and structural integrity of the coating; their corrosion resistance determines their thermal stability and durability in the marine environment [7]; and their high thermal and electrical conductivity helps inhibit local temperature rise, delay the corrosion process, and provide conditions for cathodic protection [10-15]. Therefore, systematic research on the mechanical behavior, corrosion resistance mechanism, and thermal-electrical conductive properties of graphene-modified anti-corrosion coatings has become a key path to improve the service capability of materials in extreme environments and promote the development of related technologies.

4.2.1 Mechanical properties

During coating preparation and curing, external forces and temperature changes can easily induce microcracks, providing channels for corrosive media penetration and leading to local corrosion. Graphene can effectively inhibit crack propagation within the coating and enhance its toughness, strength, and other mechanical properties. Its toughening and crack-resistant mechanisms mainly include three aspects: Firstly, stress at the crack tip causes debonding at the matrix-graphene interface and induces secondary microcracks around or between graphene layers, dissipating fracture energy through interface morphology evolution; strong interfacial adhesion further enhances coating toughness; under higher stress, graphene itself may tear, absorbing additional energy and delaying crack growth. Secondly, when a crack propagates to a graphene nanosheet, it may bend or deflect, leading to crack path changes such as deflection, pinning, bridging, or branching, effectively hindering further crack extension. Thirdly, graphene can influence the crystallization behavior of polymers, enhancing the overall toughness and strength by altering crystallinity and crystal structure [12].

4.2.2 Corrosion resistance

Graphene, as a reinforcing phase material, is the thinnest known two-dimensional layered anti-corrosion material. It effectively blocks the penetration of corrosive media such as water, oxygen, and chloride ions on metal surfaces, exhibiting unique protective effects. By dispersing graphene within organic coatings, a dense physical barrier layer can be formed, significantly improving the coating's corrosion resistance.

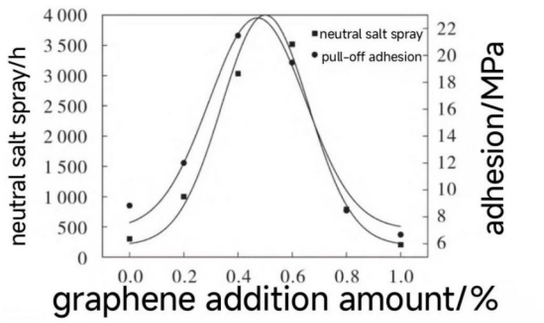

Figure 5 Gaussian fitting of neutral salt spray resistance and adhesion force

Cui Dingwei et al [3]. investigated the anti-corrosion mechanism of graphene-zinc powder coatings by improving pull-off adhesion, reducing zinc powder content, and employing microscopic analysis. Neutral salt spray test results showed that under constant zinc powder content and Pigment Volume Concentration (PVC) in the dry film, the coating's neutral salt spray resistance and adhesion initially increased gradually and then decreased sharply with increasing graphene addition. Gaussian fitting of the experimental data (Figure 5) revealed that although the optimal values for corrosion resistance and adhesion did not completely coincide, both reached superior levels at a graphene addition of 0.5%, significantly better than other addition amounts.

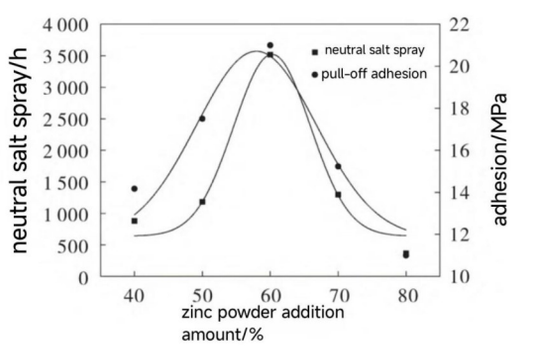

Figure 6 Gaussian fitting of neutral salt spray resistance and adhesion force (varying zinc content)

Under the conditions of a fixed graphene addition amount (w(graphene) = 0.5%) and pigment volume concentration (PVC = 55%), with the increase of zinc powder addition amount, the neutral salt spray resistance and adhesion of the coating both show a trend of first increasing and then decreasing (Figure 6). The Gaussian fitting results show that when the zinc powder addition amount is 60%, both performance indicators achieve better values, which are significantly superior to other proportions.

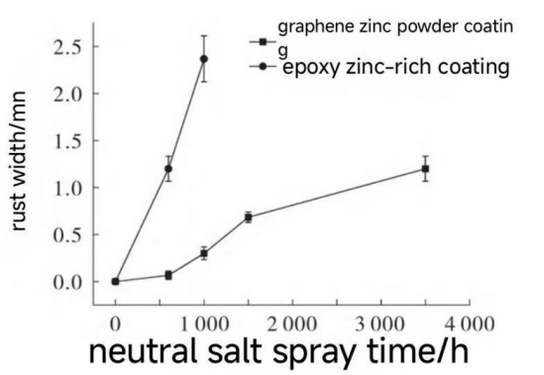

Figure 7 Corrosion width-time curve

According to the optimal ratio (w(graphene) = 0.5%, w(Zn) = 60%, PVC = 55%), the graphene-zinc powder coating prepared using the process described by Cui Dingwei et al. exhibited excellent anti-corrosion performance. Its neutral salt spray resistance time reached 3500 hours, with an average rust width of only 1.5 mm. In contrast, the epoxy zinc-rich coating performed acceptably at 600 hours, showed significant blistering at 1000 hours (average rust width 2.4 mm), and severe blistering by 1500 hours. Pull-off adhesion tests showed that the adhesion of the graphene-zinc powder coating was 22.8 MPa, significantly higher than the 7.8 MPa of the epoxy zinc-rich primer.

In summary, graphene content and zinc powder content are key factors affecting the performance of this composite anti-corrosion coating. When the ratio is appropriate, the coating's adhesion and corrosion resistance are significantly superior to other ratios.

4.2.3 High thermal and electrical conductivity

Corrosion is a heterogeneous chemical or electrochemical reaction between a metal and its surrounding medium, accompanied by the transformation of the metal from a ground state to an oxidized state. This process is an exothermic reaction with a decrease in Gibbs free energy. If the reaction heat cannot be dissipated in a timely manner, it will cause local heat accumulation, accelerate corrosion, and impair the mechanical properties of the metal such as strength, toughness, and plasticity. Graphene exhibits an extremely high in-plane thermal conductivity, reaching approximately 5000 W/(m·k) at room temperature, which is significantly higher than that of traditional thermally conductive materials like copper, aluminum, and diamond. Its excellent thermal conductivity stems from its highly ordered lattice structure, strong carbon-carbon covalent bonds, and low phonon scattering rate. The long average free path of phonons and the two-dimensional quantum confinement effect further endow it with efficient thermal management capabilities at the nanoscale. In anti-corrosion coatings, graphene can promote the rapid dissipation of corrosion reaction heat, effectively inhibit local temperature rise, and delay the corrosion process. Graphene also possesses outstanding electrical conductivity, with an electron mobility of up to 15000 $cm^2/(V·s)$ at room temperature. Moreover, its carrier concentration can be flexibly adjusted through electric fields or chemical doping, demonstrating tunable electrical behavior ranging from metallic to semiconducting. The high electrical conductivity originates from its unique Dirac cone band structure, which makes charge carriers behave as massless Dirac fermions, thereby achieving high mobility and low resistivity. This characteristic enables graphene to form an efficient conductive network in the coating, improve electrochemical contact, and provide uniform and effective cathodic protection for metal substrates.

4.3 Main influencing factors for graphene anti-corrosion coatings

There exists strong van der Waals force between graphene sheets, which makes them prone to agglomeration. This leads to uneven dispersion of graphene in the coating matrix; graphene nanosheets tend to agglomerate and also have poor compatibility with most organic polymer matrices. Aiming at the problems of difficult dispersion and easy agglomeration of graphene in the resin matrix, improving its dispersibility in the matrix is crucial for enhancing the anti-corrosion performance of the coating. Chemical modification methods are usually used to functionalize graphene, so as to improve its interfacial compatibility and dispersion stability. The dispersion state, orientation and aspect ratio of graphene-based nanofillers have a significant impact on the anti-corrosion performance of the coating. In addition, the size of graphene sheets also directly determines the barrier protection performance of the coating.

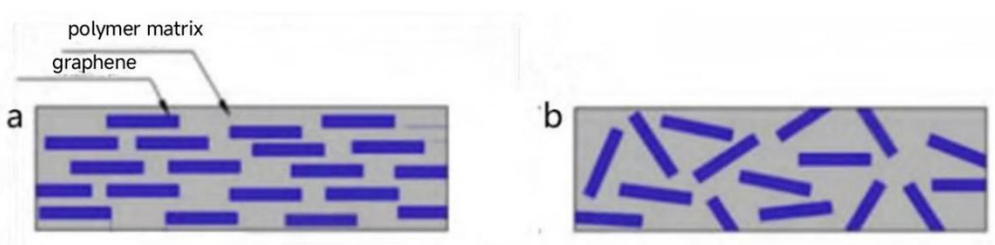

Figure 8 Mathematical models of horizontally ordered and disordered graphene in a polymer matrix

Inspired by the structure of nacre in biological shells, some studies have proposed that if the ordered arrangement of two-dimensional materials can be achieved in the coating matrix, it will significantly increase the overlapping area of the sheets and the efficiency of stress transfer, thereby effectively enhancing the barrier properties, corrosion resistance, and mechanical properties of the coating. Coatings with such a highly ordered layered structure exhibit obvious anisotropy, and their insulating properties perpendicular to the layered direction further enhance the overall anti-corrosion effect.

5 Conclusion

This paper reviews the research progress of using graphene as a reinforcing phase to improve the performance of anti-corrosion coatings required in fields such as port construction, cross-sea bridges, undersea tunnels, ship engineering, and deep-sea exploration. The analysis reveals that graphene is difficult to disperse in solid powder anti-corrosion coatings. Moreover, as most graphene materials are at the nanoscale or microscale, they are light and thin. When applied to solid powder anti-corrosion coatings, issues such as difficult spraying and poor adsorption of graphene on the surface of metal substrates arise, which affect the performance enhancement of anti-corrosion coatings. Among these issues, uniform dispersion and disordered random arrangement are the main limiting factors. Currently, efforts to lift this limitation primarily rely on combining the process characteristics of different preparation methods and attempting new preparation technologies. As a novel preparation technology, organic small molecule-modified graphene provides a brand-new option for the preparation of graphene-modified anti-corrosion coatings.

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