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SURFACE MODIFICATION OF COMPOSITE COATING FOR MARINE APPLICATION: A SHORT REVIEW

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Abstract

Corrosion is a prevalent phenomenon that significantly contributes to the deterioration of materials in offshore applications. The aggressive nature of marine corrosion is primarily attributed to the high salt content and the low electrical resistivity of seawater. While corrosion cannot be entirely eliminated, its reaction can be slowed down. Applying protective coatings is an effective and widely utilized method to protect metal surfaces from corrosion. These coatings act as a protective barrier that separates the metal from its surrounding environment, effectively retarding the corrosion rate. According to ISO 12944, the most commonly used generic coating systems for marine service include alkyd, acrylic, ethyl silicate, epoxy, vinyl ester, polyurethane, polyaspartic, and polysiloxane. The latest innovations in marine coatings still employ a layer-by-layer coating method, involving primer coats, intermediate coats, and top coats, depending on the desired thickness. Marine structures exposed to atmospheric conditions are commonly coated with one or two layers of epoxy. For enhanced performance, a more expensive system involving a layer of zinc-rich primer, followed by epoxy and aliphatic polyurethane coatings, may be utilized. Coating systems for atmospheric conditions are frequently employed in intertidal and splash zones. On the other hand, immersion zones of marine structures are typically coated with one or two layers of 100% solid epoxy, or three layers of solvent-borne epoxy. The use of a single polymer as a generic coating has limitations. Incorporating fillers is a widely employed technique to enhance the characteristics of polymers, thereby transforming them into composites. In marine coatings, fillers are still limited to glass flakes and powder. Poor dispersion and agglomeration might reduce the effectiveness of fillers in the matrix, which decreases the adhesion properties. The fillers must be surface-modified before application. This review provides a comprehensive and critical analysis of the current research status of composite coatings that serve as candidates to be used in marine coating applications.

Keywords: *Corrosion, marine coating, composite, surface modification*

1. INTRODUCTION

Metal is the primary raw material utilized in product design and construction structure within the manufacturing industry, where material processing techniques play a crucial role. It is important to conduct a thorough study of metallic materials before they are used in industrial applications, to maximize their efficiency and effectiveness [1]. Steel and alloys are commonly employed materials in marine construction, playing a crucial role in the fabrication of marine structures. Steel undergoes classification to ensure its appropriateness for specific applications in the marine environment. The classification of steel allows for the identification of its unique properties, facilitating a better understanding of its potential uses. Steel is classified based on various factors, including composition, manufacturing techniques, finishing methods, microstructure, strength, heat treatment, and product form [2].

The ocean-based economy encompasses a diverse array of industries, including fishing, coastal tourism, shipping, offshore energy, marine manufacturing, maritime infrastructure, and ocean-related services [3]. Among these diverse activities, the offshore energy and mineral resources sectors stand out as the largest industries

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that heavily rely on metal for constructing platform structures, docks, pipelines, and ships.

Energy is one of the elements needed to realize a prosperous country. Energy is also a determinant of a country's sustainable development. Therefore, the need for energy is a must, and its sustainability must be maintained [4]. The utilization of offshore structures is paramount for the energy and economic sectors of multiple countries, as these structures primarily serve as drilling platforms to extract precious oil and gas reserves from beneath the ocean floor [5].

Materials, particularly metals, often encounter environments that induce deterioration. This process, known as corrosion, occurs when metals react with their surrounding environment, leading to changes in their properties and a significant reduction in performance [6]. The damage inflicted by corrosion on offshore structures is influenced by various factors. Statistical data shows that marine corrosion is responsible for approximately 30% of failures in ships and marine machinery, resulting in annual costs surpassing $1.8 trillion [7]. The marine environment's high salinity and low electrical resistance exacerbate its corrosive nature [8]. The presence of chloride in seawater can cause the depassivation of several metals and alloys, including stainless steel, aluminum alloys, and titanium alloys, even in the absence of oxygen. Furthermore, chloride can also be found in the marine atmosphere, posing a risk of corrosion to materials and structures that are not submerged [9]. Corrosion occurs when a material, typically a metal or alloy, undergoes a chemical or electrochemical reaction with its surroundings, resulting in the deterioration of the material and its properties. This degradation can be categorized as either chemical or electrochemical, depending on the environmental factors involved. Additionally, corrosion can be classified based on the surface morphology of the affected material or the underlying causes that contribute to the corrosion process. The two most prevalent types of corrosion are uniform corrosion, which affects the entire surface uniformly, and localized corrosion, which occurs in specific areas [10]. Corrosion is a thermodynamic system of metal and its environment, which strives to reach equilibrium. The system is in equilibrium when the metal has formed oxides or other more stable chemical compounds [11]. Corrosion cannot be stopped completely, but the reaction can be slowed down. Various methods can be employed to prevent corrosion, such as treating the metal surface, modifying the corrosive environment, regulating the electrochemical reaction that triggers corrosion, attacking corrosion with corrosion, applying protective coatings to the metal, and alloying the metal [2]. However, corrosion prevention methods using coatings are widely used and popular to protect metals from corrosion [12]. Coating serves as an effective strategy for corrosion protection by establishing a barrier that effectively isolates the metal from its surrounding environment [13]. This specialized layer is specifically designed to hinder any interactions between the substrate and destructive environments such as moisture, water, and other chemical compounds [14]. Safeguarding crucial infrastructure against the ravages of corrosion is a paramount concern in numerous industries. In the marine, pipelines and structure platforms face relentless challenges from harsh conditions and persistent exposure to corrosive elements, leaving them highly susceptible to the destructive forces of corrosion [15]. Applying protective coatings to these structures doesn't just stop leaks, it also extends their useful life and keeps them structurally sound. Coatings that guard against corrosion are essential in the maritime industry [16]. The salty ocean environment poses a constant threat to the durability of ships, platforms, and other marine structures. The constant contact with corrosive seawater causes these vessels and facilities to degrade at a faster rate compared to structures in less harsh conditions. This relentless exposure to the corrosive nature of the marine environment accelerates the corrosion process, leading to the need for more frequent maintenance and repair [17]. A protective coating is essential for preserving assets from corrosive surroundings, extending their useful life, lowering maintenance costs, and guaranteeing operational safety [18]. These protective layers effectively shield structures in diverse marine environments, such as atmospheric, submerged, splash, and tidal zones [12].

The protection against corrosion is accomplished through several processes, such as the shielding effect, providing a sacrificial layer, and the ability to repair itself. The shielding effect develops a protective covering that isolates metals from external conditions, blocking any direct contact or interaction between the metal and corrosive agent [18]. Creating a protective layer will obstruct impurities and other damaging elements into the underlying substrate [19]. Sacrificial protection works by adding a metal with a higher electrochemical potential than the metal protected into the coating [20]. Due to their high reactivity, they are designed to be corroded before the metal they protect. The self-healing properties are activated through the addition of additives or materials that have the ability to mend themselves when faced with minor damage or scratches occurring [21].

Corrosion poses a significant challenge to the long-term economic success and environmental responsibility of a wide variety of industries, and the associated economic impacts, safety risks, and environmental damage highlight the urgent need to develop effective corrosion prevention methods. Protective coatings serve as an important primary protection mechanism, safeguarding materials, infrastructure, and ecosystems from the harmful effects of corrosion.

To tackle these obstacles, a range of techniques have been devised. The main aim of these methods is to improve particular characteristics like corrosion tolerance, wear tolerance, surface hardness, electrical insulation, thermal insulation, water repellency, and wettability [22]. These methods offer different approaches for applying coatings onto different substrates. Vapor-based chemical deposition is a process where gaseous materials interact to form a solid coating on a surface. This involves the chemical reactions of vapor-phase components, which culminate in the creation of a solid layer on the substrate. Physical Vapor Deposition employs physical processes like evaporation or sputtering to deposit a thin layer onto the substrate. Microarc Oxidation generates a ceramic coating through the electrochemical oxidation of metal. Thermal spraying entails projecting a liquid or semi-liquid material onto the substrate's surface. The sol-gel technique forms a layer through the hydrolysis and condensation of a precursor solution. The polymer coating is first applied in a liquid state, and then undergoes a hardening process to become a solid protective layer [23]-[24]. This text explores techniques used to alter the surface properties of fillers, aiming to strengthen the bond between fillers and matrices. The impact of surface modification techniques on the effectiveness of composite coatings was investigated.

2. Generic in Marine Coating

The marine environment is characterized by a higher presence of corrosive elements compared to natural conditions [24]. The high concentration of chloride particles in ocean water is the main factor behind this phenomenon. These chloride ions can penetrate and weaken the protective layer that shields the substrate, making them susceptible to localized corrosion, such as pitting [26]-[27]. Reliability and durability are critical for steel structures that are exposed to environmental attacks, particularly those situated close to the coast or off-shore (marine environments). It is therefore vital that the protective coating applied can provide protection from harmful elements. ISO 12944 is a set of instructions and recommendations on the various types of paints and protective coatings suitable for safeguarding steel structures. This international standard outlines the essential requirements and best practices for selecting, applying, and maintaining effective anti-corrosion systems for steel-based constructions. The extent to which the steel structure is exposed to corrosive conditions determines the level of protection required and the paint or coating system that is recommended for use [27].

Coating formulations typically consist of solvent, resin, pigment, filler, and additives. Once administered onto the base metal, these formulations create a seamless, uniform coating that safeguards against cracking and structural deterioration caused by stress, water infiltration, and natural wear and tear. For protective coatings to be deemed effective, they must exhibit minimal permeability, excellent corrosion resistance, and high adhesive to warrant their performance [28].

The Society for Protective Coatings serves as the preeminent authority and resource in the protective coatings industry, providing essential knowledge and guidance on preparing surfaces, choosing the right coatings, applying, and following environmental and safety rules. Within the marine coatings sector, manufacturers offer a diverse range of generic coating options tailored to the specific requirements of various marine applications [29]. This short article only discusses coating selection and application.

Sailors navigating on the wide sea often rely on protective coatings to shield their vessels from the sun's harsh rays and the corrosive marine environment. These coatings commonly feature single or double-layer epoxy, with the number of layers determined by the desired thickness of the protective barrier. Additionally, an aliphatic polyurethane layer is added to shield the epoxy from the harmful ultraviolet rays of the sun. In cases where the structure is not subjected to direct sunlight, two or more layers of epoxy may be employed. Alternatively, a slightly more expensive system comprising a zinc-rich primer coat, an epoxy coat, and an aliphatic polyurethane coat could provide enhanced performance in harsher environments.

Protective coatings intended for exposure to atmospheric conditions are often applied in areas where water regularly contacts the surface, like the shoreline and areas subject to splashing, to shield against deterioration. Within these specific regions, it is common practice to employ a flake-filled epoxy coating to enhance resistance to impacts and abrasions. Furthermore, the application of Monel coating, which extends around 20 feet beneath the water's surface, serves the purpose of inhibiting the growth of marine fouling organisms and preventing corrosion on the steel substrate.

Marine structures often have immersion areas that are protected by either a single, double, or three layers of solid epoxy. Epoxy coatings that have been cured with polymeric amide solvent are renowned for their exceptional resistance to water and their capability to withstand partially cleaned steel surfaces. Coal tar epoxy coatings, which are renowned for their superior water resistance, are commonly used in a single or double-layer coating system for surfaces that are submerged [29].

According to ISO 12944, the marine setting is classified as having the most severe level of corrosiveness, denoted as Cx extreme. To shield structures from deterioration in this setting, it's crucial to use a coating that boasts robust mechanical attributes, endurance against abrasion, insulating capabilities, and chemical resilience. Commonly utilized materials for marine coatings include epoxy, polyurethanes, vinyl esters, and alkyds [27]. The latest innovations in marine coatings still use a layer-by-layer coating method (primer coats, intermediate coats, and top coats) depending on thickness. In marine coatings, fillers are still limited to glass flakes and powder [30]-[31]

Epoxy resins are renowned for their remarkable ability to offer effective barrier protection in various environments [31]. The hydrophilic nature of epoxy, attributed to the presence of polar epoxy groups, can be influenced by the combination of hydrophilic or hydrophobic polymers, thereby affecting the equilibrium properties of the resulting polymer [32]. The efficacy of epoxy as a coating is influenced by the presence of water, consequently impacting the overall performance on coating performance [33]. Epoxy is a highly popular thermosetting resin that finds extensive use due to its exceptional physical and chemical characteristics. These qualities encompass the lack of volatile components throughout the curing stage, the capacity to cure across a broad temperature spectrum, and the potential to attain regulated cross-linking. In the past century, epoxy has become a staple in the coatings industry or structural applications. This is largely due to their exceptional capabilities, which are further enhanced when paired with aliphatic amine curing agents [34]. Epoxy is widely acknowledged as the most extensively utilized anti-corrosion coating due to its exceptional mechanical characteristics, wear resistance, insulating capabilities, and stability in both acidic and alkaline environments [35]-[36]. These qualities make epoxy a preferred choice for various applications, as it can withstand extreme conditions. However, epoxy coatings do possess certain limitations, when cured coating can create tiny holes, weakening the coating. Additionally, these coatings may not withstand environmental factors well, becoming less durable and adhering poorly over time, potentially leading to deterioration [37]-[38]. Improving the effectiveness of coatings is essential in resolving the difficulties at hand. Ensuring these coatings operate optimally is key to addressing the prevailing concerns. Several methods can be employed to improve epoxy properties, such as polymer synthesis, incorporating additives, and utilizing new curing agents [39]. The incorporation of fillers has also emerged as a common technique to enhance polymer properties and transform them into composites [40]. In the realm of marine coatings, fillers are currently limited to glass flakes and powder [29]-[30]. Incorporating supplementary fillers enhances both the frictional and structural attributes of composite coatings [41]. GO, CNT, and nanoparticles are commonly used as fillers to reinforce these layers. The improvements in properties are credited to the interactions between the filler substances and the surrounding material, which involve covalent, hydrogen, and physical bonds [42]. The enhanced mechanical characteristics of composite coatings play a crucial role in their ability to inhibit the formation and spread of cracks, ultimately leading to improved coating performance [43]. However, the filler must be uniformly dispersed within the polymer matrix to achieve these improved properties. In cases where the dispersion is inadequate, agglomeration occurs, weakening the bond and causing separation between the filler and matrix, a phenomenon known as particle debonding. The effectiveness of the coating is significantly influenced by its adhesive characteristics. The quality of the coating is determined by the connection between the coating and the underlying surface. When the coating and the surface integrate seamlessly, it indicates strong adhesion, resulting in a smooth transition. Conversely, poor adhesion is reflected in a rough transition between the coating and the surface [42].

3. Surface Modification

Determining the effectiveness of modifying the filler's surface can be accurately done by studying how well it interacts with the surrounding matrix material. Improving the filler's ability to blend seamlessly with the matrix is crucial for enhancing the corrosion resistance of the composite. Analyzing the WCA (water contact angle) and surface energy provides important insights into the hydrophilic (water-attracting) nature of the fillers [44]. Several existing surface modification techniques are available.

3.1 Physical Vapor Deposition

Applying thin film coatings is achieved through a method called PVD. This process involves the manipulation of materials at the atomic level within a vacuum environment. While PVD shares similarities with CVD (chemical vapor deposition), there are notable distinctions between the two methods. In PVD, solid precursors or materials are utilized for the deposition process, whereas CVD introduces the precursor in a gaseous form into the reaction chamber [44]-[45]. PVD presents numerous benefits. It enables the application of extremely thin layers of materials, generating coatings with visually appealing characteristics. Additionally, these coatings demonstrate improved resistance against deterioration from corrosion and physical wear [46]-[47].

3.2 Chemical Vapor Deposition

Chemical processes happen right on or close to the surface of a hot material in a method called CVD. The vapor transforms and solidifies, creating a physical substance that settles out of the gaseous state. The resulting solid materials can exhibit diverse structures, such as single crystals or thin layers. Through careful control of different factors, such as the composition and temperature of the underlying surface, the setup of the gas mixture fueling the reaction, and the speed at which the gas flows, it becomes achievable to design materials with a wide range of physical, friction-related, and chemical characteristics [48]-[49].

CVD offers several notable benefits, such as its capacity to enhance corrosion and wear resistance. Additionally, it enables the deposition of diverse materials with distinct microstructures. Furthermore, CVD can be conducted under low and ambient pressures [50]-[51]. However, there are certain limitations associated with this process. It requires the use of a heat-resistant substrate and an ultra-high vacuum environment. Additionally, there is a tendency for some wastage of the coating material during the CVD process [50]-[52].

3.3 Micro-Arc Oxidation

MAO is an innovative electrochemical technique that utilizes rapid micro-arc discharges to create porous ceramic coatings on various transition metals and their alloys, including aluminum, titanium, magnesium, and zirconium. This process involves subjecting the metal surface to high-voltage electrical discharges in an electrolyte solution, resulting in the formation of a ceramic layer with unique properties [53]-[56]. When the applied voltage exceeds the dielectric breakdown voltage of the ceramic/oxide layer, a micro-arc discharge is initiated. This phenomenon occurs due to the high voltage causing the breakdown of the dielectric material, leading to the discharge of electrical energy in the form of a micro-arc [57]-[60]. The distinctive feature of MAO lies in its ability to provide a porous substrate-based oxide layer, which cannot be achieved through conventional manufacturing techniques. This unique characteristic sets MAO apart from other traditional methods, offering a specialized oxide layer that enhances the material's properties and performance in various applications [62].

3.4 Electrodeposition

Electrodeposition coating is an electrochemical process that allows for the formation of a uniform metallic coating with an even thickness distribution on a conductive substrate. The selection of the substrate and deposition material is crucial as they serve as the cathode and anode within the electrochemical cell [63].

3.5 Sol-gel

The sol-gel technique is a commonly employed method for the deposition of thin layers, typically less than 10 millimeters in thickness. This approach, in contrast to conventional thin film fabrication techniques, offers enhanced control over the chemical composition and microstructural properties of the deposited layers. Additionally, the sol-gel method facilitates the production of uniform films, reduces the solidification temperature requirements, and provides the advantage of utilizing simpler and more cost-effective equipment [64].

3.6 Thermal spray

Thermal spray coating is a technique where manufacturers liquefy specially designed parts by applying intense heat like plasma, electricity, or burning chemicals. This transforms the materials into a protective layer. These layers are created by melting specific components through the application of heat from sources [64]-[66]. The thermal spray coatings can be classified into five main sections based on the different energy sources utilized during the procedure. These categories encompass energy derived from flammable gases, the power of motion, electrical sparks, radiation, and liquid fuels. Each of these energy forms holds a pivotal part in shaping the overall efficiency and excellence of the thermal spray coating procedure.

Thermal coating can generate layers with diverse thicknesses, ranging from a mere 20 micrometers to several millimeters. This method stands out for its ability to achieve high deposition rates over large surface areas, surpassing other coating processes. Researchers have investigated an assortment of covering substances. The chosen coating substance is carefully heated until it transforms into a semi-liquid or molten form, ready to be applied. The metal arrives in powdered, bar-shaped, or wire-like forms, and is then rapidly accelerated, typically at speeds between 100 and 1500 meters per second, towards the target surface. This high-speed motion causes the metal to break apart into tiny droplets, which then cling to the target, building up the desired coating layer [68].

Diverse methods have been engineered to modify the characteristics of material surfaces, including PVD, CVD, sol-gel processing, MAO, electroplating techniques, thermal spraying, and several additional approaches. These techniques offer various benefits, such as enhanced protection against corrosion and wear, increased hardness, the ability to insulate electricity and heat, water-repelling properties, and improved wetting characteristics [22]. Each of these surface modification techniques has its characteristics depending on the application.

Table 1. Advantages and disadvantages of various surface modification techniques

Method	Advantages	Disadvantages	Ref
PVD	• Adjusting corrosion and visual appeal, while also boosting durability and applying a thin protective layer, can be effectively achieved and modified.	• High vacuum conditions are necessary, as abrasion can compromise the corrosion resistance of materials in polymer deposition applications, making damage control a challenging task.	[45], [46], [47], [48]
CVD	• Shielding against wear and tear, blending various substances with unique inner structures, and operating in both low and standard air pressures are critical factors in many industrial endeavors and uses.	• A high level of vacuum is required, along with a substrate that can withstand high temperatures, and minimal wastage of the coating material is necessary for this process.	[49], [50], [51], [52], [53]
MAO	• Exceptional hardness and outstanding corrosion resistance, combined with a porous framework that is well-suited for use in biological settings, as well as a diverse array of porosity levels spanning the entirety of the material's thickness.	• Primarily associated with valve metals such as aluminum, titanium, tungsten, chromium, and others.	[54], [55], [56], [57], [58], [59], [60], [61], [62]
ELD	• Applications for ornamentation, resistance to corrosion, high-temperature resistance, and abrasion.	• The effectiveness is heightened when paired with conductive metals.	[63]
Sol-gel	• Affordable.	• Manage the thickness and slow cycle time.	[64]
Plasma spray	• Restoration of polymers, rubber, metals, and engineered fibers through surface repair. Enhanced substrate adhesion, corrosion and wear resistance, and non-stick coating. Eco-friendly method for fiber	• Low-temperature techniques involving substrate surface modification necessitating heat energy are used on stuff unreactive at natural pressure. Extended exposure to plasma results in fiber damage through the creation of	[69]

	surface modification without environmental pollution.	deeper holes on the fiber surface. Procedures at low temperatures induce alterations on the substrate surface, necessitating a heat source, and are employed for substances unreactive under atmospheric natural pressure.	
Cold spray	● In contrast to alternative thermal spraying techniques, this method is both straightforward and cost-effective.	● Not particularly useful in extreme conditions.	[66]
Arc wire spray	● A protective coating on the internal surface of the engine block ensures resistance against wear and corrosion.	● Limited to utilizing conductive materials and wires for coating purposes.	[67]
Warm spray	● Ideal for substances prone to oxidation when exposed to elevated temperatures or for heat-vulnerable.	● Exceedingly severe settings offer no value.	[65]
Nano-particle growth	● The filler's surface remains undamaged by the process. The high ratio of length to thickness leads to enhanced shear resistance. The performance gets better, and corrosion resistance is increased due to the exfoliated filler.	● The process of filler growth can incur significant costs. Agglomeration of filler material is a potential issue that may arise. The maintenance of a high vacuum poses challenges and can be costly, particularly for certain types of fillers that necessitate surface modification.	[70], [71], [72], [73], [74], [75], [76], [77]

4. COMPOSITE COATING

According to ISO 12944, the most commonly used generic coating systems in marine applications include AK (alkyd), AY (acrylic), ESI (ethyl silicate), EP (epoxy), PUR (polyurethane), PAS (polyaspartic), and PS (polysiloxane) [27]. Single-polymer coating systems are inherently limited in their applications due to certain constraints. To enhance the sliding and strength characteristics and tackle these drawbacks, extra materials like fillers are blended into the coating compositions. However, polymer films exhibit permeability to O_2 and H_2O over time, with instances where the rate of H_2O and O_2 diffusion on layers exceeds the threshold necessary to trigger the corrosion of a metal substrate [78]. Incorporating inorganic fillers is a viable approach to enhancing the anti-corrosion characteristics of organic coatings [79]. Fillers come in various forms, from carbonous to a combination of monomers, ceramics, light metals, silicate minerals, TMS, and nanofillers [80].

Polymer composites incorporate various types of filler materials that serve distinct purposes. There are two primary categories: reinforcing fillers and lubricant fillers. Reinforcing fillers are materials that possess greater strength and modulus in comparison to the plastic base material, thereby enhancing mechanical properties. Fibers and nanofillers have been extensively utilized as reinforcing fillers in various studies. Common examples of conventional reinforcing fibers include carbon fiber, glass fiber, and silica fiber [80]-[81]. Additionally, CNTs have exceptional properties which are highly suitable for enhancing the strength of polymer composite materials, primarily due to their unique one-dimensional structure and remarkable strength [80]-[82]. Montmorillonite, a type of two-dimensional nanoclay, is also widely employed to strengthen the physical properties of polymers. This clay-like substance helps improve the durability and performance of a wide range of plastic-based products [84]. Furthermore, a wide range of nanofillers, such as aluminium oxide, silicon dioxide, zinc oxide, silicon carbide, and copper are suitable for serving as strengthening components in polymer-based composites. Lubricant additives are substances that are designed to reduce the friction between the components in polymer-based materials. Some common examples of these lubricant additives include Teflon, carbon, MoS_2, phosphorene, Au, and Cu. These materials work by lowering the resistance between the moving parts, which helps to improve the overall performance and efficiency of the composite materials [84-86]. The incorporation of certain reinforcing fillers can enhance the composite performance. This is illustrated by the improved properties of epoxy resin when silicon dioxide and carbon are added [88].

CNTs offer advantages because of their capacity to diminish friction and offer anti-corrosion characteristics, in addition to their pivotal role in diverse tribological applications. Fullerene, graphene, carbon nanotubes, and nanodiamonds are four prominent types of carbon nanomaterials that have been employed in coating applications [88]-[89].

Certain silicon-based minerals, such as montmorillonite and kaolin, possess thin, layered structures with high aspect ratios and substantial interfacial areas. These minerals can be chemically bonded to polymers, enhancing the rigidity and resistance to deformation of the polymer matrix [83],[90]-[91]. Silicon dioxide has been extensively utilized as a filler in various polymer systems, both in synthetic and natural forms. The addition of silica enhances the polymer's stiffness and resistance to deformation, owing to its remarkable stability under temperature changes and its inherent structural strength. However, unlike talc or mica particles, which have a low aspect ratio and form flakes or plates, silica filler particles do not share this characteristic. Consequently, unless the silica particles are minuscule, adding them to the polymer leads to a comparatively small surface coverage to interact. As a result, the reinforcement provided by silica filler is less significant compared to platy fillers. Nevertheless, when the size of the filler particles is reduced to sub-micron dimensions, the composite resin exhibits exceptional and desirable properties. While sub-micron silica and barium sulfate have been employed as nanofillers, organically modified clay-based nanofillers offer the most remarkable properties at a relatively low cost. This is primarily due to their extremely high aspect ratios, which exceed 1000, in contrast to the aspect ratios of common fillers, which are typically 100 or less. This high length-to-diameter ratio of clay particles contributes to improved dimensional stability compared to conventional microfillers. However, a significant challenge arises in the dispersion of nanofiller particles, as their complete dispersion within the polymer matrix during melt processing is difficult or even impossible to achieve. Consequently, the actual properties of nanocomposites may only partially realize their potential or theoretical properties. To overcome this issue, a common approach involves modifying the surface of the clay particles with quats or other. This surface modification process facilitates the desired exfoliation of the clay particles, resulting in the creation of delicate layers with nanometer-scale thickness in the polymer matrix [93].

Ceramic nanoparticles, including SiO_2, Si_3N_4, SiC, TiO_2, and Al_2O_3, demonstrate superior mechanical characteristics under various temperature conditions. Consequently, they are frequently utilized as reinforcing components to improve matrix performance [93]-[97].

The enhancement properties of the composite layer are heavily associated with the filler phase. This is accomplished through various characteristics, including their arrangement, dimensions, form, permeability, and surface modification on the fillers. The bonding between matrix and filler is vital in boosting the protective film. Numerous research approaches have been dedicated to enhancing the performance of resin composites by investigating the correlation between organic resins and inorganic fillers. Typically, fillers in composite materials are treated with chemical agents resulting in strong chemical bonds between separate components and improving water resistance. The hydrophobic or hydrophilic nature of a coating holds significant importance as it allows for the evaluation reaction between surface layers and surroundings. This interaction is vital in improving mechanical properties, wear resistance, and retarding the degradation process. Furthermore, it facilitates the transition of stress from a more flexible organic matrix to a highly rigid inorganic filler [98]-[99].

The filler was modified not only as a linkage and to minimize stress development during polymerization but also to enhance hydrophobic or super hydrophobic properties. Here, the use of various fillers synthesized with a surface modification method is considered. Therefore, this part will recap the development of composite coatings with generic materials commonly applied in marine coatings.

Table 2. Summary effects of filler addition and modification method on corrosion resistance of composite coatings

Generics	Fillers	Modification method	Environment	Achievements	Ref

Epoxy	ZrO_2 particle size 15 nm	Sol-gel with APS (amino propyl trimethoxy silane)	Immersed 3.5wt.% NaCl	The inclusion of 2-3% zirconium dioxide nanoparticles significantly improved the corrosion resistance. This enhancement was due to the improved barrier properties and ionic resistance.	[101]
Epoxy	Mixing ZrO_2 nanoparticle and Cloisite 30B particle size 13 μm	Ternary ammonium salts	Immersed 3.5wt.% NaCl	The addition of zirconium oxide and nanoparticles to the coating systems enhances the coating's anti-corrosion properties. The nanoparticles enhance the coating's barrier and electrical resistance, resulting in better corrosion protection.	[102]
Epoxy	Mixing ZrO_2 particle size 15 nm with Closite 30B particle size 2-13 μm	ZrO_2 with APS, Closite 30B with ternary ammonium salt	Neutral salt spray test	The addition of nano zirconia slightly improves the mechanical properties of the epoxy coating. This is due to the formation of clay clumps that slow down the curing process and reduce the density of polymer crosslinks. The creation of nano-scale voids around the clay buildup also contributes to the enhancement.	[103]
Epoxy	Mixing GO particle size 300 μm with cloisite 15A particle size 13 μm	Nanoclay modified with quaternary alkyl ammonium salt	Immersed 3.5wt.% NaCl	The coating showed very high electrical resistance, over 10^{10} ohm·cm^2, even after being immersion for 18 weeks. This shows the coating is very stable. Other tests like salt spray, pulling, and electrical tests also showed the coating performed better when the clay in it was mixed in better.	[104]
Alkyd	Clay based on MMT particle size of 7-9 μm	Dimethyl dehydrogenated tallow ammonium chloride	Immersed 3wt.% NaCl	The Scanning Electron Microscopy and AFM analysis showed that the nanoclay particles were well-dispersed in the coating. The AFM images confirmed the coating's nanoscale stability, even after prolonged exposure to salt water. This suggests the composite coating had enhanced stability. The Electrochemical Impedance Spectroscopy results also demonstrated that the composite coating provided better corrosion protection compared to other barrier coatings. This improvement is attributed to the flat montmorillonite sheets in the coating, which prevented defects and reduced the transport of water and corrosive substances.	[105]
Epoxy	Mixing bentonite with TiO_2	CTAB (cetyl trimethyl ammonium bromide)	Without corrosion test	The addition of a 5% filler component, at a concentration of 0.1 M CTAB, led to an improvement in the mechanical characteristics of the material. Additionally, the water absorption test demonstrated a direct correlation between the increase in filler content and the material's water absorption capacity.	[106]
Polyurethane	Mixing silica particle size 14 nm with carbon particle size 595 μm	Unmodified	Salt spray test	Increasing the carbon and silica content of a material can improve its corrosion resistance, as demonstrated by various analytical techniques like FTIR, TGA analysis, optical observations, and salt spray testing. These methods have consistently shown that a higher ratio of carbon to silica results in enhanced resistance against corrosion.	[107]

Polyaniline	SiO_2	Unmodified	NaCl 1M	Adding a 10% SiO_2 guarantees the highest corrosion resistance. The initial corrosion rate is 0.00896 mm/year, but it drops to 0.00024408 mm/year after exposure.	[108]
Epoxy	Metalloam	Unmodified	5wt.% NaCl Salt spray test	Metalloam addition did not significantly impact corrosion resistance. However, adding 15% metalloam increased adhesion by 22.5%	[109]
Polyaniline	rGo (reduced graphene oxide)	Unmodified	Potentiodynamic polarization with I^- (iodide) / I_3^- (tri-iodide) based electrolyte	The addition of reduced rGO (graphene oxide) to PANi (polyaniline) coatings significantly reduces the corrosion rate. The PANi/rGO coating with the highest rGO concentration 8wt.% had the lowest corrosion rate at 0.2 mm/year and a protection efficiency of 80.3%. This high performance is due to the passivation effect, which blocks corrosive ions from reaching the substrate surface.	[110]
Epoxy	ZnO particle sizes 910.6 nm and 189.3 nm	Stearic acid	Immersed 3.5wt.% NaCl	9% filler provides optimal results. Modification of the ZnO filler using stearic acid was increase water contact angle. Effect protection coating through barrier effect and hydrophobic effect. Micropores in epoxy composite coatings will be filled by ZnO fillers. Surface modification of the ZnO filler reduces the corrosion rate due to the hydrophobic nature of stearic acid, so the electrolyte tends not to make contact with the modified filler.	[111]
Polyurethane	-	Sol-gel Catecholamine	Immersed 3.5wt.% NaCl	The addition of catecholamines to a sol-gel coating improved its corrosion resistance and adhesion to a waterborne polyurethane layer. The adhesive strength increased from 1.74 MPa to 2.75 MPa. After 120 days of immersion, the coating's resistance to corrosion also improved significantly, as shown by a large increase in the charge transfer resistance from $4.9 \times 10^4\ \Omega\cdot cm^2$ to $1.7 \times 10^7\ \Omega\cdot cm^2$.	[112]
Epoxy	Mixing 2D MXene nanosheets with ZnO QDs (quantum dots)	ATPES (3aminno propyl triethoxy silane)	Immersed 3.5wt.% NaCl	The coating made with a mixture of F-MXene@ZnO and a water-based epoxy polymer is very good at preventing corrosion. When 0.50% of this mixture was added to the water-based epoxy, the coating was able to resist corrosion much better than the neat epoxy. Even after being immersed for 30 days, the coated surface was still 3 times better at preventing corrosion compared to the neat epoxy.	[113]
Epoxy	Nano-alumina	Doped with PB (polybenzopyrrole)	Immersed 3.5wt.% NaCl	The PB/AN@ZE 0.25% film is very good at protecting against corrosion. Tests showed it was able to protect 97.14% of the surface after being submerged for 24 days. The film also stayed strong, with an impedance value of $1.48\times10^9\ \Omega.cm^2$ even after 24 hours submerged. This means the film is excellent at preventing corrosion and holding up well in water.	[114]
Epoxy	Graphene oxide	Doped with GPTMS	Salt-mist	The f-GO-epoxy coated samples were tested and showed they are very good at	[115]

				protecting against corrosion. The tests used electrical measurements to check how well the coating resisted corrosion. They also did a pull-off test to see how well the coating stuck to the surface. The results showed the f-GO-epoxy coating was very effective at preventing corrosion.	
Vinyl ester	Two-dimensional MXene nanosheets	MPS (3methacryloxy propyl trimethoxy silane)	Immersed 3.5wt.% NaCl	The materials in the composite layer work well together. The different parts are connected in a strong way, which makes the layer better at preventing corrosion. The materials are mixed nicely, which makes it harder for harmful things to get through to the surface underneath. This helps the composite layer be more resistant to corrosion.	[116]
Epoxy	Two-dimensional lamellar MXene nanosheets	One-step dopamine-triggered with polyethyleneimine	Immersed 3.5wt.% NaCl	The WEP coating is very good at preventing corrosion. This is because the coating has special fillers that are spread out well, it creates a strong barrier, and it works well with the surface it is on. Even after being submerged for 30 days, the WEP coating with a small amount of MXene was still able to stop corrosion very well. The coating was only about 55 micrometers thick, but it was able to stop corrosion twice as well as the regular WEP coating without the MXene.	[117]
Epoxy	ZIF-67 containing 2-mercatobenzothiazole	PFTS (perfluorooctane trethoxy silane)	Immersed 5wt.% NaCl	The PHBN-ZIF@MBT composite material showed strong barrier properties and the ability to release corrosion inhibitors. After immersion, the coating became much more hydrophobic, with the contact angle increasing from 78.35° to 116.8°. The adhesion strength also improved by 82.6%. Electrochemical Impedance Spectroscopy analysis indicated the composite layer maintained high impedance values even after 28 days submerged, demonstrating effective long-term corrosion protection.	[118]
Epoxy	Micro/nano-sized silica	Sol-gel with ZIF-8 (2-methylimidazole zinc salt)	Immersed 3.5wt.% NaCl	The ZIF-8@SiO2/APTES/EP coating is very good at preventing rust and corrosion. In a saltwater solution, it was able to stop 99.99% of the corrosion. Even after being in the water for 72 hours, it continued to work very well at preventing corrosion. Tests showed that this material formed a thick protective layer on the metal surface. This layer is very resistant to corrosion and is also very stable chemically.	[119]
Epoxy	Basalt	Grafting ZnO	Immersed 3.5wt.% NaCl	The special coating is very good at killing bacteria. This is because the zinc oxide (ZnO) layer in the coating has a very tight structure and sticks very well to the surface. The ZnO layer also makes it harder for the base layer to move around in the resin. This helps the base layer spread out evenly, which makes the coating better at preventing corrosion.	[120]

Vinyl ester-Epoxy	GO (graphene oxide)	Grafting vanillin and silicon	Immersed 3.5wt.% NaCl	The composite material achieved its best performance when 0.1% more of a certain component was added. While the electrical conductivity was still low enough to be considered an insulator, the material saw a 38% increase in breaking strength, a 65.7% increase in contact angle, and 99.03% anti-corrosion efficiency.	[121]
Polyurethane	MMT (montmorillonite)	TA (tannic acid)	Immersed 3.5wt.% NaCl	The coating on this material keeps its strong protection even after being immersed for 50 days. The coating is about 3 times better at protecting the material than the original uncoated material. The coating can also repair small physical damage to itself by using a special chemical reaction when heated. This means the coating is very good at preventing corrosion and lasting a long time.	[122]
Epoxy	Graphene	Solution intercalation technique	Immersed 3.5wt.% NaCl	Adding 1% graphene improves the polymer coating's protective abilities. This is due to the graphene nanoparticles being well-dispersed and distributed. Increasing graphene from 0.5-3% boosts the contact angle and reduces water absorption. But higher concentrations lead to graphene clumping, which decreases corrosion resistance.	[123]
Epoxy	Glass fibers	Modified with 3-Triethoxy silyl propyl amine and grafting with phytic acid and Zn^{2+}	Immersed 3.5wt.% NaCl	The PA-Zn^{2+}-m-GF/WEP coating is very good at stopping wear and corrosion when it has 20% of a special material added to it. After being used for 1000 times, the coating only got about 30% thinner. Even after being immersed for 144 hours, it was still very good at stopping corrosion, with a high electrical resistance.	[124]
Epoxy-PES	CNPs grain size 30nm	Unmodified	NIR laser irradiation testing	The PES/EP-CuS coating exhibited an impressive ability to prevent corrosion and restore the integrity of the material while in use, thus highlighting its resilient self-repairing capacity. This coating demonstrated remarkable efficacy, underscoring its capability to withstand corrosion and repair any resulting damage.	[125]
Epoxy	Hexagonal boron nitride	Triple-functional filler enhances	Immersed 3.5wt.% NaCl and Salt Spray Test	The Ce^{3+}&PANI/h-BN composite coating was found to be very good at preventing corrosion. It was 55.5% and 89.67% effective at stopping corrosion. After being immersed for 40 days and salt spray test, the composite coating was 13 times better at blocking electrical signals than the neat epoxy coating. This shows the composite coating had much better anti-corrosion protection than the neat epoxy coating.	[126]
Polyurethane	Cerium oxide and graphene oxide particle size 0.2–10 µm	Straight forward spraying method	Immersed 3.5wt.% NaCl	Fixes any small holes or problems in the coating, so the metal is fully protected from corrosion. The CeO_2 also releases special ions that create a new layer that protects against corrosion even more. This makes the coating very strong against corrosion.	[127]

				Even after being immersed for 27 days, the coating is still working very well.	
Epoxy	rGO and BTA@HMS	CTAB (cetyl trimethyl ammonium bromide)	Immersed 3.5wt.% NaCl	The coating made of different materials is 4 times better at stopping corrosion than just neat epoxy. BTA@HMS in the coating helps fix any damage to the coating. This makes the coating much better at protecting the surface underneath from corrosion. The protection against corrosion is much stronger, going from 60 $K\Omega \cdot cm^2$ to 3410 $K\Omega \cdot cm^2$.	[128]
Epoxy	Chitin & Chitosan nanoparticle	Unmodified	Immersed 3.5wt.% NaCl	The coating that had 2% chitin nanoparticles in it was stronger and better at sticking to things. Tests also showed that the coating with 2% chitin and chitosan nanoparticles rusted less, was better at holding heavy things, and could hold twice as much weight before breaking.	[129]
Epoxy	Ti_3C_2 MXene 2D materials	Dopamine and loading corrosion inhibitor	Immersed in saline media	The tests showed that coatings with special ingredients to prevent rust and corrosion worked better than regular epoxy coatings without those ingredients. The coatings with the special anti-corrosion ingredients performed better in the tests.	[130]
Epoxy	Nano silicon dioxide	PFDTES via facile spray-coating	Immersed 3.5wt.% NaCl	The self-repairing coating demonstrates remarkable corrosion resistance, as evidenced by an almost eightfold increase in Rct (charge transfer resistance) when compared to untreated Q235 carbon steel substrates. This indicates a significant enhancement in the coating's ability to prevent corrosion. Furthermore, the coating exhibits excellent sustainability in corrosion protection, as it effectively restores its original anti-corrosion ability, ensuring long-lasting protection against corrosion.	[131]
Epoxy	Graphene	MAO coating and spin coating EP	Immersed 3.5wt.% NaCl	The test results showed that the composite layer had a very high corrosion resistance. After being soaked in liquid for 40 days, the layer had a low-frequency modulus of $6.76\times10^{10}\ \Omega \cdot cm^2$. This is about 100 times higher than the resistance of a normal epoxy coating. This means the composite coating is much better at preventing corrosion compared to a neat coating.	[132]
Alkyd	PANI-Fe_2O_3	Unmodified	Immersed 3.5wt.% NaCl and 1M HCl	The coating made of polyaniline-iron oxide and alkyd resin is better at protecting mild steel from rust compared to just using the neat alkyd. This is because the polyaniline-iron oxide in the coating helps to create a protective layer on the steel and also fills in gaps, making it harder for rust to form. Studies have shown that this special coating is more effective at preventing corrosion than the neat alkyd coating.	[133]
Polyurethane	Graphene	N-Methyl-2-pyrrolidone via ultra sonication	Immersed 3wt.% NaCl and salt spray	The coating made of PU (polyurethane) with 1% graphene flakes had stronger sticking power, about 2.3 MPa, compared to neat PU. The coating with 2% graphene	[134]

			test 5wt.% NaCl	had very good protection against corrosion. After being immersed for 150 days or exposed to salty air for 2500 hours, it still had a high resistance of 2.7 x $10^{\wedge 10}$ Ohm-cm^2, which means it was very good at preventing corrosion.	
Epoxy-Acrylic	Graphene nanoplatelets	HT-PDMS (hydroxyl-terminated polydimethylsiloxane)	Water contact angle and surface adhesion test	The coating with 1% graphene had the highest water contact angle of 99.75 degrees, meaning it was very water-resistant. Adding graphene to the coating made it degrade at a lower temperature. More graphene also meant the coating had less cross-linking, which made it perform a bit worse. This was likely because the graphene particles clumped together in the coating.	[135]
Polysiloxane	Silica nanoparticle and PS-grafted	HDTMS (hexadecyl trimethoxy silane)	Acid and alkali resistance test	Inclusion of silica within the composition of the coating results in heightened surface roughness and a significant enhancement in its hydrophobic properties. Following a rigorous abrasion test consisting of 90 cycles, the water contact angle on the coating can surpass 150°. Moreover, this particular coating demonstrates exceptional durability against the corrosive effects of both acids and alkalis.	[136]
Ethyl silicate	Nickel oxide nanoparticle	Zinc-rich	Immersed 3.5wt.% NaCl	The coating with 3% nickel oxide had much less corrosion and wear compared to the neat ethyl silicate coating. It also was much better at preventing corrosion, going from 3069 to 16482 ohm-square centimeters. This is because the tiny NiO particles in the coating can slow down the dissolving of the zinc and make the coating stronger by filling in small holes and creating complex paths that are hard for corrosion to get through.	[137]
Polysiloxane	SiO_2 and ZnO	PFDTMS (perfluoro decyltrimethoxysilane)	Immersed 3.5wt.% NaCl and Water contact angle test	The incorporation of SiO_2 nanoparticles made the surface of the coating very water-resistant, or "superhydrophobic". The water didn't stick to the surface at all. When measured, the water made a very high angle of 165.3° ± 1.5° on the surface. And the water just rolled off the surface at a very low angle of only 2.2° ± 0.7°. Electrochemical Impedance Spectroscopy tests showed the coating was almost 4 times better at preventing corrosion compared to neat polysiloxane coating. The addition of SiO2 particles made the surface very water-resistant and much better at preventing corrosion.	[138]
Vinyl ester	2D MXene nanosheets	Unmodified	Immersed 3.5 wt.% NaCl	The incorporation of a 0.1wt.% MXene into vinyl ester significantly improved the layer resistance and apparent impedance, with increases reaching 330%. The hydrophobic MXene nanosheets acted as a protective shield, obstructing the penetration of harmful electrolytes and creating a more complex diffusion	[139]

				pathway, thereby enhancing the overall corrosion protection performance.	
Novolac vinyl ester	Silicon nitride particle size <20 µm	DFHMA (dodecafluoroheptyl methacrylat)	Immersed 10 wt.% NaCl	By blending 8wt.% DFHMA with 3wt.% β-Si_3N_4, the resulting nanocomposite coating exhibited effective corrosion protection and desirable hydrophobic characteristics.	[140]
Vinyl ester	Titanium dioxide and graphene	Triggering MEKP and accelerator of cobalt naphthalate	Immersed 3.5 wt.% NaCl	The addition of filler additives to VER films helps disperse cobalt, improves the crystal structure, and boosts corrosion resistance. This is due to the creation of IPNs within the substance. Incorporating a TiO_2 and G hybrid reinforcement into the VER matrix also significantly enhances the corrosion resistance and adhesion properties of the final film.	[141]
PVB-Epoxy	Graphene oxide	Silane coupling agent KH-550	Immersed 3.5 wt.% NaCl	The original PVB/EP coating had a corrosion resistance of 84.03% and a contact angle of 60.43 degrees. After adding 0.89% GO (graphene oxide), the corrosion resistance improved to 92.57% - an 8.54% increase. The contact angle also increased significantly to 114.66 degrees, indicating a major change in the coating's surface properties.	[142]
PDMS	g-C_3N_4 (graphitic carbon nitride)	Tannic acid	Immersed 3.5wt.% NaCl	The composite coating showed excellent corrosion resistance, maintaining very high electrical impedance even after 28 days submerged. This coating also had the ability to self-heal when exposed to light, fully recovering within just 3 hours.	[143]
Polyurethane	Zr and Ni based amorphous alloy powder	Composite metal powder	Immersed 3.5wt.% NaCl	Incorporating amorphous alloys has significantly improved the corrosion resistance of coatings. An analysis found that a 50% Zr-based amorphous alloy composition showed the best performance in reducing corrosion, outperforming the other compositions tested.	[144]
Polyurethane	Graphene oxide	Unmodified	Immersed 3.5 wt.% NaCl and salt spray test	Adding 0.75% graphene oxide to polyurethane coatings significantly improved their anti-corrosion properties. The coatings had very high electrical impedance that didn't decrease even after self-healing from scratches. The coatings also showed excellent corrosion resistance, withstanding a 20-day salt spray test without any visible signs of corrosion.	[145]
Epoxy	Nanoclay MMT	Unmodified	Immersed 0.5M NaCl	Enhanced protection against corrosion can be observed in copper coated with EPMC when subjected to a sodium chloride solution. The incorporation of 5% MMT clay content in the EPMC coating further enhances the level of protection, resulting in the highest level of resistance to corrosion.	[146]
Epoxy	ZrO_2 nanoparticle	APTES (3-amino propyl triethoxy silane)	Immersed 3.5 wt.% NaCl	Epoxy's corrosion resistance can be improved by adding a specific amount of APTES to modify nano ZrO_2. The composite layer with 2% nano ZrO_2 by	[147]

				mass has an impressive impedance of around 1.0 × 10^{5} Ω.cm^2, resulting in superior corrosion resistance.	
Epoxy	ZIF-67@DTMS Nanoparticle	DTMS (dodcyltrimethoxysilane)	Immersed 3.5 wt.% NaCl	Adding ZIF-67@DTMS nanoparticles to epoxy coatings improves their corrosion resistance and adhesion. The nanoparticles form strong bonds with the epoxy and fill in any gaps, creating a better barrier against harmful substances. This enhances the overall anti-corrosion performance of the coating.	[148]
Epoxy	ZIF-8	PPy (conductive polypyrrole)	Immersed 3.5 wt.% NaCl and salt spray test	The addition of fillers significantly enhances the corrosion resistance of epoxy coatings. This improved protection comes from the combined effects of passive and active corrosion-fighting mechanisms. The PPy@ZIF-8 particles act as passive nanofillers that shield the surface, plus they can self-heal by generating a protective iron oxide and zinc hydroxide layer on the steel.	[149]
Epoxy	Fluorinated graphene	ZIF-8 and Triton X-100	Immersed 3.5 wt.% NaCl	The coating modified with FG had better mechanical properties, more resistance to wear, and longer-lasting protection against corrosion compared to the unmodified EP coating. However, the limited compatibility between FG and the resins made it difficult to significantly improve the corrosion resistance.	[150]
Epoxy	Graphene oxide	Maleic acid diamine	Immersed 3.5 wt.% NaCl	The addition of 0.3% M-GO into a water-based epoxy coating provided excellent anti-corrosion properties. After being submerged for 96 hours, the composite coating showed very high impedance, extremely low corrosion current, and nearly 99.9% protection efficiency against corrosion	[151]
Epoxy	h-BN and DA	Dual self-healing effect BTA and PDA	Immersed 3.5 wt.% NaCl	The addition of BPCT nanosheets to waterborne EP coatings improves the coatings' ability to block harmful substances and self-heal any defects. This results in exceptional corrosion resistance for the coated materials.	[152]

5. CONCLUSION

Marine environments exhibit unique characteristics that differentiate them from other natural conditions. These environments are known to possess elevated levels of corrosive elements, such as extreme humidity and aggressive atmospheres. This makes alloys susceptible to localized corrosion. The Society for Protective Coatings provides valuable recommendations on coating selection and application.

The traditional marine coating approach involves a layer-by-layer application of primer, intermediate, and top coatings. The selection of these coatings is determined by the desired thickness required for the marine structures. For atmospheric protection, a common practice is to apply single or double layers of epoxy. For enhanced performance, a more expensive system using zinc-rich primer, epoxy, and polyurethane can be used. Coating systems specifically designed for atmospheric conditions are generally utilized in intertidal and splash zones. Submerged areas are typically coated with single, double, or triple-layer solid epoxy.

The limitations of using single polymers as generic coatings have led to the widespread adoption of incorporating fillers to enhance their characteristics and transform them into composites. In the realm of marine coatings, the options for fillers are currently restricted to glass flakes and powders. The primary concern regarding heavy-duty marine coatings is their adhesive properties. Even the best coating materials are useless if they don't stick well to the surface. That's why it's crucial to carefully formulate the entire coating system to ensure strong adhesion. In the production of composite coatings, the filler material must be uniformly dispersed into the matrix. Insufficient dispersion of fillers can result in agglomeration, impeding the matrix from fully bonding with other fillers and consequently diminishing the adhesion properties. The remedy for this predicament lies in modifying the filler with a coupling agent. For instance, the inclusion of 2D fillers like nanoclay can enhance the barrier effect and mechanical properties of polymers. However, a limitation associated with nanoclay is its layered silica structure, which requires modification with quaternary ammonium compounds or other coupling agents to achieve intercalated or exfoliated nanocomposites.

The incorporation of fillers into polymers serves a pivotal role in augmenting their characteristics, particularly with respect to corrosion resistance, in comparison to unfilled polymers. However, it is paramount to meticulously evaluate the filler type, particle size, and composition. Certain fillers may necessitate surface modification prior to incorporation. By reducing the filler particle size to the submicron range, the composite material can exhibit enhanced and distinctive properties. Conversely, an excessive filler composition could result in agglomeration issues before the polymer is fully cured.

This review provides a thorough and critical examination of the development of composite coatings and their potential use for marine applications. The purpose of this concise review is to contribute to exploring new filler materials and surface modification techniques that could improve the performance of composite coatings.

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