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#### Review

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# Progress of material degradation: metals and polymers in deep-sea environments

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Abstract: Given the critical need for ocean exploration, improving the durability of materials in the deep-sea has become a paramount concern. The harshness of deep-sea, such as high pressure, variable seawater flow rates, and corrosive media, lead to premature aging and failure. This work examines the utilization of metals and polymer coatings in deep-sea applications, detailing the characteristics of the deep-sea and its influence on these materials. In particular, chloride ions in seawater pose significant hazards to metal corrosion, which is the main reason for metal failure. Then, the degradation process and the latest research advances of various materials in the deep-sea environment are summarized, and the failure mechanism of the metal/ coating system in the deep-sea is analyzed. It was found that the failure of polymer coatings can be divided into three processes, and adding an appropriate amount of fillers to the coating (such as adding 0.2% graphene to water-based polyurethane) can extend the service life of the coating. Finally, the development trend of the company in the future is predicted. It has guiding and reference significance for the study of the failure behavior of metals and polymers in the deep-sea environment.

**Keywords:** deep sea; metallic materials; polymer coatings; failure behaviour; failure mechanisms

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#### 1 Introduction

The deep sea, home to a wealth of strategic resources and energy crucial for human societal advancement, has emerged as a 'new frontier' contested by nations worldwide. Pursuing deep-sea resources has spurred the rapid evolution of deep-sea engineering equipment and technologies. In recent years, many deep-sea devices have been deployed extensively for resource exploration, military defense, and scientific research in the ocean depths. The foundation of such equipment rests on materials like metals, alloys, and various non-metallic substances. The trend towards developing deep-sea equipment that is larger in scale, capable of reaching greater depths, designed for extended operations, all-ocean exploration, multifunctionality, and autonomous operation has escalated the demand for materials with superior core performance, large-scale manufacturability, long-term durability, broad temperature range adaptability, and multifunctional capabilities (Guo et al. 2008; Hou 2004; Vizentin and Vukelic 2022). The long-term reliability of materials in deep-sea environments is essential for crafting high-quality, advanced materials and equipment (Li et al. 2023a; Lin et al. 2019). Material and component failures not only shorten the lifespan of marine engineering projects, disrupt normal equipment operation, increase maintenance and repair costs, and incur significant economic losses but can also lead to catastrophic incidents, resulting in severe environmental pollution, ecological harm, and potentially jeopardizing human lives and property (Khan et al. 2022; Xia et al. 2022).

Contrasting with the shallow marine setting, the deep-sea environment presents a complex and severe challenge, with factors such as high pressure, salinity, humidity, elevated levels of dissolved CO<sub>2</sub> and O<sub>2</sub>, and increased flow velocity intensifying the corrosion of deep-sea materials and diminishing their lifespan (Guo et al. 2006). Although considerable progress has been made in the past decade in developing polymer protective coatings (Figure 1), research on the corrosion mechanisms affecting deep-sea materials remains limited. Consequently, comprehensively investigating the corrosion mechanisms impacting deep-sea

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materials subjected to high-pressure and corrosive environments and evaluating their protective coatings is crucial for advancing materials with greater resistance to both pressure and corrosion. This endeavor aims to extend the operational life of deep-sea engineering equipment and boost service safety and reliability. This paper discusses the characteristics of the deep-sea environment and the corrosive challenges it presents, reviews recent advancements in the study of corrosion and aging failure of metals and polymer coatings used in deep-sea equipment, and anticipates future research directions in understanding the failure mechanisms of deep-sea materials.

### 2 Deep-sea environment and the resulting failures

#### 2.1 Deep-sea environment

The marine environment, characterized by its complexity and severity, demands that the physical and chemical properties of materials be meticulously analyzed in relation to their specific surroundings. This detailed examination is essential to understand and address material failure. considering the unique challenges posed by different marine zones, as shown in Figure 2. The marine environment is segmented into the shallow sea, continental shelf, and deep sea areas. The deep sea, typically defined as areas with water depths exceeding 200 m, exhibits significant variations in

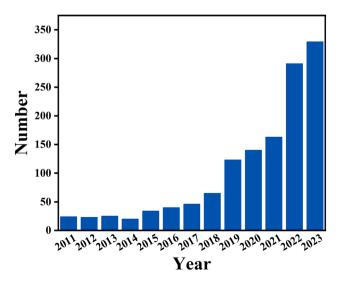


Figure 1: Number of research papers related to polymer anti-corrosion coatings published per year from 2011 to 2023. The statistics were obtained from the "Web of Science" with the search term "polymer anti-corrosion coating".

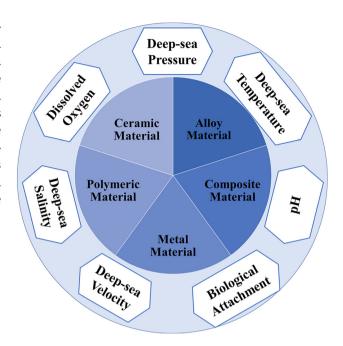


Figure 2: Relationship between deep-sea corrosivity factors and material corrosion failure.

physicochemical properties and factors leading to material failure compared to surface waters. Influences such as high pressure, varying concentrations of dissolved oxygen, salinity, temperature fluctuations, light availability, pH levels, the velocity of seawater flow, and microbial activity crucially impact the corrosion and aging processes of materials utilized in deep-sea conditions.

- Pressure: pressure serves as a crucial metric for differentiating between deep-sea and shallow-sea environments. Research indicates that, with constant seawater density, salinity, and dissolved oxygen levels, seawater pressure escalates by 1 MPa with every 100-m increment in depth. This heightened pressure significantly accelerates the electrochemical reaction rates of metals in service under these conditions (Duan et al. 2019a). Consequently, in systems where polymer coatings are applied to metal, the diffusion of corrosive agents, such as water, Na<sup>+</sup>, Cl<sup>-</sup>, etc., through the coating is accelerated, affecting the durability and integrity of
- Temperature: as ocean depth increases, temperature generally decreases due to several factors. The absence of direct sunlight in deeper waters primarily limits heat transfer. Additionally, the presence of the thermocline – a distinct oceanic layer where temperature decreases sharply with increasing depth - further accentuates this temperature decline. Consequently, temperatures in deep-sea environments typically stabilize near freezing, ranging from approximately

- $0-4\,^{\circ}\text{C}$ . The influence of temperature on corrosion rates is well-documented. According to the basic principles of thermodynamics, in most cases, a decrease in temperature will reduce the rate of chemical reactions. which also applies to seawater corrosion reactions. Thus, in the colder conditions of the deep sea, metal corrosion rates are generally reduced (Melchers 2004). Seawater velocity: the influence of seawater velocity on metal corrosion is multifaceted. For metals capable of forming a protective passivation layer, low seawater velocities facilitate oxygen diffusion, aiding in the formation of this layer and thus mitigating corrosion (Wang 2005). Conversely, high seawater velocities can erode the passivation film, increasing metal corrosion. Multiple factors, including wind, topography, tides, and the temperature-salinity structure, influence seawater velocity variation with depth. Generally, seawater velocity is greatest at the surface due to the direct influence of wind. As depth increases, the velocity typically decreases. However, there can be localized variations depending on specific areas and conditions.
- Dissolved oxygen concentration: oxygen concentration generally decreases with increasing sea depth due to reduced light penetration, limiting photosynthesis and reducing water layer mixing. For most materials, an increase in seawater's dissolved oxygen concentration enhances the oxygen diffusion on the surface of the material. This allows dissolved oxygen to rapidly reach the cathodic areas of the corrosion interface, accelerating the metal's corrosion rate (Zhou et al. 2010). Therefore, as the depth of seawater increases, the effect of dissolved oxygen on the material will weaken. pH: the pH of seawater varies with depth, influenced primarily by biological activity, water mixing, and chemical processes. At the surface, the pH of seawater is typically higher, ranging from approximately 8.1–8.3. This elevated pH is attributed to active photosynthesis in surface waters, where algae and phytoplankton absorb carbon dioxide and release oxygen, thereby increasing the pH. As depth increases, light availability diminishes, resulting in reduced photosynthetic activity. Concurrently, the carbon dioxide produced by biological respiration and the decomposition of organic matter accumulates, leading to a gradual decrease in the pH of seawater. These slight variations do not directly impact the corrosion of materials. Nonetheless, a decrease in pH correlates with a decreased concentration of dissolved oxygen. This connection implies that while pH changes themselves might not directly affect corrosion, the resultant

- changes in oxygen concentration could indirectly influence the corrosion behavior of materials in seawater environments.
- Salinity: as the depth of seawater increases, the salinity (6) of seawater increases slightly. The average salinity of seawater is approximately 3.5%, which significantly enhances its conductivity compared to freshwater sources such as rivers. This heightened conductivity, in turn, accelerates metal corrosion in seawater environments. In such settings, corrosion manifests at the microscopic level, where tiny battery-like reactions occur, and at a macroscopic scale, leading to more substantial battery-type corrosion. Consequently, this environment substantially intensifies corrosion activity.

#### 2.2 Failure in the deep-sea environment

Aging failure is the deterioration of materials due to environmental influences, resulting in resource consumption, environmental pollution, and engineering accidents (Neuhaus et al. 2017). Aging failure not only consumes resources but pollutes the environment and causes engineering accidents to a certain extent. Since human activities have involved the ocean, there have been countless catastrophic accidents caused by marine engineering failures yearly (Křivý 2022; Sun 2023). For instance, in July 1988, the explosion of the Piper Alpha platform in the UK's North Sea resulted from a rupture in the compression tubes and gas leakage, claiming 167 lives and injuring 66. This tragedy reduced UK oil and gas production by 12 %, resulting in an annual economic loss of £9.5 million. In April 2010, the Deepwater Horizon drilling rig in the Gulf of Mexico suffered a blowout and subsequent explosion due to inadequate quality checks post-cementing, resulting in 11 fatalities, 17 injuries, and a massive oil spill of 4.9 million barrels. In November 2013, the corrosion and thinning of pipelines at the intersection of Sinopec's Donghuang pipeline and a drainage ditch caused a severe accident. In November 2013, the corrosion and thinning of the pipeline at the intersection of Sinopec's Donghuang pipeline and a drainage ditch ruptured the pipeline, triggering an explosion and leakage that resulted in 62 deaths, 136 injuries, and economic losses of up to 750 million yuan. In December 2016, the oil drilling platform of Azerbaijan's National Oil Company in the Caspian Sea collapsed due to fatigue damage from long-term cyclic loading of components, resulting in the collapse of an offshore platform, killing almost 30 people. More recently, in June 2023, the Titan deep submergence vessel imploded

under water pressure at 3,800 m, killing all five onboard. As the marine industry advances, the demands on offshore drilling platforms, pipelines, ships, submarines, and other structures intensify. Corrosion-related economic losses globally amount to 2–4% of the gross national product annually, with marine corrosion representing a third of these losses, emphasizing the urgent need for improved materials and maintenance practices to mitigate aging failure and its devastating impacts (China Shipowners Mutual Assurance Association 2023).

In conclusion, the reliability of marine engineering materials and components is crucial for ensuring the continuous expansion of the national economy. It is essential to investigate the degradation of these materials' protective properties over time and understand their failure mechanisms. By doing so, we can improve the durability and safety of marine engineering materials and structures, reduce the frequency of catastrophic accidents, and extend the operational lifespan of marine projects.

# 3 Corrosion failure of metal materials in deep-sea

As key materials for deep-sea engineering facilities, metallic materials are widely used in equipment such as mobile deep-sea workstations, deep-sea exploration platforms, and deep submersibles. However, the complexity and harshness of the deep-sea environment places higher demands on the reliability of material structure and function, where any potential material failure may lead to catastrophic accidents. Therefore, understanding and mitigating the corrosion of metallic materials in the deep sea is imperative. Researching their corrosion dynamics and implementing effective anti-corrosion strategies are essential for ensuring the safety and longevity of deep-sea projects and are critical in averting catastrophic failures.

#### 3.1 Corrosion failures of aluminum alloys

As the exploration of the ocean progresses from shallow to deep sea, aluminum alloy has emerged as a preferred lightweight material for marine equipment due to its advantageous properties. Despite its widespread use, aluminum alloy faces significant challenges in marine environments, including low wear resistance, high susceptibility to pitting corrosion, and a tendency towards corrosion cracking. These issues restrict its broader application in marine settings. Currently, research and data on the corrosion behavior of aluminum alloys in natural environments, particularly marine (characterized by salt spray, high humidity, and elevated temperatures), are limited (Peng et al. 2022; Zhang et al. 2019). Addressing the corrosion

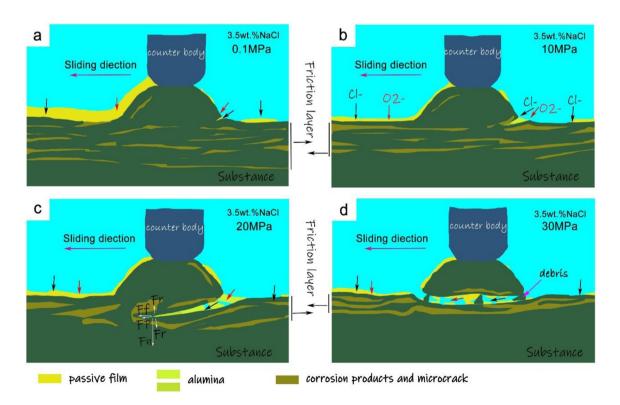


Figure 3: The possible tribocorrosion mechanism at 3.5 wt% NaCl solution. Copyright 2021. Adapted with permission from Elsevier.

of aluminum alloy is crucial for advancing the maritime industry, underscoring the need for focused research to mitigate these limitations and harness the full potential of aluminum allovs in these sectors (Canepa et al. 2018; Zhao et al. 2021).

The 5000 series aluminum alloys, comprising Al, Cu, Mg, Fe, Si, and Mn, exhibit excellent corrosion resistance, making them ideal for marine engineering applications. This series is utilized in marine facilities, including amphibious aircraft and aircraft carriers (Canepa et al. 2018; Duan et al. 2022). The 5A06 aluminum alloy stands out for its superior corrosion resistance. Research by Duan et al. (2023b) has shown that in deep-sea conditions of the western Pacific, the 5A06 alloy primarily experiences pitting corrosionat at the depths of 500, 800, 1,200, and 2,000 m, and its resistance will be improved at deeper depths. This improvement suggests that factors such as hydrostatic pressure and reduced dissolved oxygen concentration at increased depths positively affect the alloy's corrosion parameters, including average corrosion rate, maximum pitting depth, and corrosion area ratio. However, local corrosion remains a significant challenge, potentially reducing the alloy's service life and escalating maintenance costs. Further studies by Duan et al. (2019b) in the South China Sea at depths of 1,200, 2,000, and 3,000 m focused on local corrosion, a critical factor affecting the alloy's long-term utility. These insights underscore the need for ongoing research to mitigate corrosion and extend the durability of aluminum alloys in marine applications.

Junghans et al. (2015) demonstrated that hydrostatic pressure facilitates the penetration of Cl<sup>-</sup> and H<sub>2</sub>O from a 3.5 wt% NaCl solution through the surface oxide film of aluminum alloys, with this penetration effect intensifying at higher pressures. Peng et al. (2021) conducted in-depth studies on the corrosion behavior of 1,060 aluminum at depths of 1,200, 2,000, and 3,000 m using a specialized deepsea environmental test device. Through image processing and grey correlation analysis, they revealed that the corrosion process in a deep-sea environment progresses through three distinct stages: dissolution of the surface passivation film, hydroxide dissolution on the aluminum surface, and dissolution within corrosion pits. Furthering this research, Li et al. (2021c) explored the friction and corrosion behavior of 7075-T6 aluminum alloy in deep-sea conditions. They developed a tribocorrosion model for aluminum alloys, indicating that under hydrostatic pressure, the wear mechanisms shift from fatigue and delamination wear to being dominated by adhesive and stripping wear, all in the presence of corrosion. This progression underscores the complex interaction between hydrostatic pressure and material degradation, highlighting the need

for advanced materials and protective strategies in deepsea applications (Figure 3).

In summary, pitting and crevice corrosion are the primary forms of degradation observed in aluminum alloys exposed to deep-sea conditions. Hydrostatic pressure intensifies the interaction with chloride ions (Cl<sup>-</sup>) and water molecules (H2O) on the material's surface. Through a synergistic effect, this wear and corrosion result in a type of surface defect on the aluminum alloy that is not merely a straightforward accumulation of material loss (Canepa et al. 2018). Meanwhile, the incursion of seawater into these defects leads to their further expansion (MacGregor et al. 2019), exacerbating the degradation process.

#### 3.2 Corrosion failures of steel

The variety of steels encompasses carbon steel, low alloy steel, martensitic stainless steel, ferritic stainless steel, austenitic stainless steel, and duplex stainless steel, among others. In the deep-sea environment, factors including hydrostatic pressure, temperature, salinity, dissolved oxygen content, and pH change with varying seawater depth markedly influence the corrosion behavior of metal materials compared to that in shallow-sea environments. Zhang et al. (2022a) conducted a comprehensive study on the corrosion behavior of 10CrNi3MoV steel in the Western Pacific Ocean's deep-sea conditions. Their research, encompassing morphological observations, calculations of corrosion weight loss, pitting measurements, and analyses of corrosion products, revealed that the corrosion rate usually first decreases and then increases with the increase of seawater depth, and within the experimental seawater depth range, the corrosion thinning of the material in the deep-sea environment is lighter than that in the surface seawater. Notably, as water depth increases, the extent of pitting corrosion escalates. Additionally, increased Cr content results in 10CrNi3MoV steel having inferior corrosion resistance compared to ordinary carbon steel, alongside heightened local corrosion sensitivity.

Corrosion potential is critical for evaluating the corrosion and protection of metals used in deep-sea applications. Generally, materials with higher corrosion potential exhibit better corrosion resistance. In an innovative study, Ding et al. (2022a) utilized a multi-channel potential automatic acquisition device to measure the corrosion potential of 19 metal materials - including aluminum alloy, carbon steel, copper alloy, and stainless steel – under simulated deep-sea conditions at 8 MPa pressure. Their findings revealed that the corrosion potential significantly decreases over time, indicating a substantial change in potential magnitude and a corresponding decrease in material corrosion resistance. Moreover, materials with higher chromium (Cr) and nickel (Ni) content displayed more positive corrosion potentials, suggesting enhanced corrosion resistance.

Stainless steel is renowned for its exceptional corrosion resistance. As seawater depth increases, its corrosion rate typically diminishes, partly due to the formation of a dense passivation film on the stainless steel's surface. This film's integrity is significantly impacted by chloride ions (Cl-) activity in seawater, which can initiate localized corrosion. In marine environments, stainless steel predominantly experiences pitting and crevice corrosion, particularly in deep-sea settings. Liu et al. (2022) conducted a study focusing on 304 stainless steel, examining its corrosion behavior under varying hydrostatic pressures and immersion durations. Their findings, derived from in-situ electrochemical impedance spectroscopy and kinetic potential polarization curve tests, indicate that increased hydrostatic pressure diminishes the corrosion resistance of 304 stainless steel.

Furthermore, under constant pressure, prolonged exposure exacerbates its susceptibility to corrosion. Chloride ions (Cl<sup>-</sup>) are especially detrimental, as they can breach the stainless steel's passivation layer, leading to severe localized corrosion. The occurrence of pitting corrosion in 304 stainless steel is notably linked to the dissolution of MnS inclusions. In another study, Duan et al. (2019b) investigated the corrosion behavior of 460 steel in a natural deepsea environment at depths ranging from 1,200 to 3,000 m. Their research revealed that corrosion severity escalates with increasing seawater depth (Figure 4). Grey correlation analysis indicated that the corrosion rate of 460 steel is primarily influenced by deep-sea pressure and dissolved oxygen concentration, showing a positive correlation between these factors.

Galvanic corrosion, a prevalent form of localized corrosion, significantly affects metallic materials in seawater (Hu et al. 2020). Utilizing state-of-the-art techniques such as macroscopic morphology comparison, 3D confocal testing, and scanning electron microscopy, Zhang et al. uncovered substantial differences in galvanic corrosion rates among 9XX low-alloy steel, 316L stainless steel, and 5083-H116 aluminum-magnesium alloy in the demanding 3,000-m deep-sea conditions (Zhang et al. 2022b). In a detailed study, Wang et al. examined the galvanic corrosion behavior of a tri-metallic couple system, including 907A, 921A, and 980 low-alloy steels, and found that higher temperatures significantly intensify galvanic corrosion (Wang et al. 2022). This phenomenon particularly increases the corrosion rate of 907A steel, the anode material, leading to localized pitting corrosion and, consequently, a greater risk

of marine equipment failure. Conversely, the cathodic materials, 921A, and 980 steels, experience reduced corrosion rates due to the protective effects of galvanic corrosion. These findings highlight the importance of galvanic corrosion in marine environments and the necessity for effective protective measures, such as coatings and cathodic protection, to mitigate its harmful impacts.

With the development of the maritime industry, the application of ship and offshore platform components such as return pipes, steam pipes, heat exchanger pipes and exhaust systems is becoming more and more common, and the problems that arise are becoming more and more obvious. These components are highly corrosion-resistant, exacerbated by salt spray and humidity concentrations (Wu et al. 2019). In a notable research endeavor, Wu et al. explored the corrosion dynamics of 304 stainless steel alongside TiC-reinforced 304 stainless steel within a simulated marine environment heated to 650 °C. Their research unveiled that the incorporation of TiC markedly bolsters the steel's oxidation resistance. This improvement is primarily due to the oxidation of TiC, which leads to the creation of TiO<sub>2</sub>. This compound aids in the nucleation of chromium, thereby enhancing the adherence to the chromium scale and, consequently, the material's overall corrosion resistance (Wu et al. 2019). Parallelly, Zhu et al. conducted a comparative analysis of the corrosion resistance and passivation properties of a CoCrNi medium entropy alloy (MEA) versus 316L stainless steel under simulated marine conditions (Zhu et al. 2021). Their investigations showed that the CoCrNi MEA exhibited significantly enhanced corrosion resistance compared to 316L stainless steel, a disparity attributed to differences in grain size, microstructure, and the density of the surface passivation layer.

To summarize, when subjected to the harsh conditions of deep-sea environments, steel components in marine engineering are highly prone to corrosion by anions (such as Cl<sup>-</sup>) in seawater. This process detrimentally affects the steel's passivation film, leading to pronounced pitting corrosion, which can serve as a starting point for stress corrosion cracking. This issue significantly compromises material integrity. Pitting corrosion is especially prevalent in vulnerable areas of corrosion-resistant materials such as stainless steel, aluminum and its alloys, copper alloys, and titanium alloys. These areas include spots where the passivation layer is weakest, like at lattice defects, grain boundaries, and near non-metallic inclusions. In contrast, carbon steel and low alloy steel undergoes a different corrosion process in deep-sea conditions, characterized by cathodic polarization that tends to cause a more uniform corrosion distribution. This clear difference in corrosion behavior among various materials in marine settings

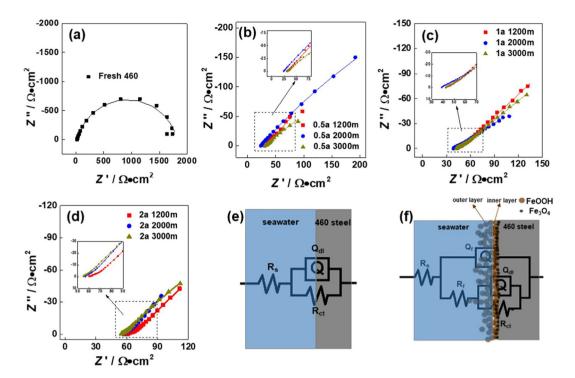


Figure 4: Nyquist plots and equivalent circuits of 460 steel with various exposure periods: (a) fresh sample, (b) 0.5a period, (c) 1a period, (d) 2a period, (e) and (f) equivalent circuits (Duan et al. 2019b). Copyright 2019. Adapted with permission from Taylor & Francis.

highlights the necessity for specific protective measures tailored to each material's unique susceptibility to corrosion.

# 4 Aging failure of polymer coatings in deep-sea

The deep-sea environment poses a unique set of physical, chemical, and mechanical challenges that make metal corrosion a common issue (Hu et al. 2019; Tian et al. 2019; Wang et al. 2021; Xia et al. 2020a). To mitigate corrosion, various metal protection strategies have been developed, including electroless plating (Liu et al. 2015), cathodic protection (Song and Shi 2014), and polymer coating (Li et al. 2021b), among others. Polymer coating stands out as a particularly effective, straightforward, and cost-efficient method (Akbarinezhad et al. 2019; Habibpour et al. 2021; Song 2010). It is a physical barrier preventing the corrosive medium from reaching the metal surface, effectively inhibiting the electron exchange between the anode and cathode. This ensures the metal's structural durability, environmental, chemical resistance, wear resistance, and toughness (Barletta et al. 2014). Gao et al. (2017) observed that under high-pressure conditions, the impedance of coatings decreases more rapidly than in atmospheric-pressure environments. High pressure tends to cause the coating fillers to

desorb more easily, compromising the integrity of the coating/metal substrate interface and enlarging the corrosion-active surface area. This accelerates coating degradation and underlying metal corrosion. Therefore, the coating must also adhere well to the substrate beyond excellent barrier properties and wear resistance. Currently, developed polymer coatings for marine corrosion prevention include those based on epoxy resin (EP), polyurethane (PU), and acrylic polymers (PAA) (Benea et al. 2020; Haeri et al. 2022; Hussain et al. 2021; Rodrigues Peruchi et al. 2021). Despite their protective capabilities, these coatings can gradually deteriorate or even detach from the substrate due to corrosion and blistering processes. Thus, understanding the failure mechanisms of polymer coatings is crucial.

#### 4.1 Aging failure of epoxy-based coatings

Epoxy resin (EP), renowned for its superior adhesion, tensile strength, chemical resistance, and durability against weathering, is a preferred polymer protective coating for marine engineering infrastructure (Bordbar et al. 2020). The degradation of pure epoxy resin-based coatings in marine environments follows a three-phase process, as delineated by equivalent electrical circuits (EEC) (Liu et al. 2013a): initially, the coating remains intact with high impedance

(Circuit A), followed by an active corrosion onset phase (Circuit B), and culminating in a rapid corrosion phase characterized by diffusion impedance (Circuit C), as shown in Figure 5.

In deep-sea environments, the high pressure significantly increases the risk of corrosive media breaching the protective coatings through inherent defects, jeopardizing the integrity of the coating-metal interface and, consequently, the entire coating-metal system (Liu et al. 2021). Extensive research has focused on integrating functional fillers like nanoparticles, fibers, and two-dimensional materials into coatings to enhance the durability of pure epoxy resins (Korde et al. 2020). Inorganic fillers, such as glass flake (Chen and Zhao 2021), montmorillonite, and silica (Khan et al. 2023), have been shown to bolster the physical barrier properties of polymer coatings by extending the path corrosive agents must traverse, thereby impeding their progress (Tian et al. 2014). Liu et al. (2013b) systematically studied the failure behavior of epoxy varnish coatings and epoxy glass flake coatings at atmospheric pressure (1 atm) and high hydrostatic pressure (35 atm) through electrochemical behavior, water transportation, wet adhesion, and mechanical properties. The result showed that the mechanical properties of the coatings were superior at 35 atm. Still, the pressure accelerated the water absorption, increased the diffusion coefficient, and the diffusion was

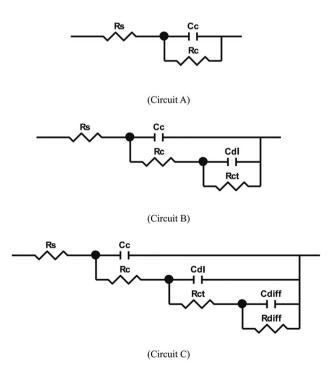


Figure 5: Equivalent circuits of the coating system for different immersion stages (Liu et al. 2013a). Copyright 2013. Adapted with permission from Elsevier.

changed from ideal Fick diffusion to S absorption of non-Fick diffusion, which altered the electrochemical behaviors and reduced the coatings' protective properties. The failure mechanism of the coatings under high hydrostatic pressure is shown in Figure 6. Echoing these findings, Tian et al. (2014) investigated how alternating hydrostatic pressures affect the durability of epoxy glass flake and high-pigment epoxy coatings in marine settings. Their work demonstrates that alternating hydrostatic pressures diminish the coatings' protective qualities and accelerate their breakdown. This deterioration is primarily caused by pressure-driven water diffusion and physical damage, which together expedite the failure of the coating, despite no change in its chemical composition.

Beyond the conventional fillers previously discussed. cutting-edge materials such as graphene, mesoporous silica (Bordbar et al. 2020), MXene, cerium oxide (Fotovvat et al. 2022; Harb et al. 2020; Joseph et al. 2021), halloysite nanotubes (HNT) (Lvov et al. 2008), and polymer microcapsules are increasingly incorporated into coatings as fillers or corrosion inhibitors. These materials are chosen for their exceptional characteristics: ultra-thin profiles, outstanding physical barrier capabilities, and extensive specific surface areas, which collectively enhance the protective performance of the coatings. They undergo specific modifications to optimize the synergy between these fillers and the polymer matrix (Shi et al. 2023). This ensures a seamless integration that bolsters the durability and efficacy of the coating, providing a robust defense against corrosion and wear in challenging environments.

Fu et al. pioneered a novel method by depositing polycaprolactone (PCL) nanofibres infused with 2-methylbenzothiazole into halloysite nanotubes (HNTs-MBT) on metal substrates (Fu et al. 2021). This approach facilitates a composite epoxy coating that immediately boosts the metal's corrosion protection, ensuring rapid and enduring resistance. Celebrated for its comprehensive utility as a corrosion-resistant filler, cerium oxide (CeO<sub>2</sub>), a rare earth oxide, has been extensively studied (Hosseini and Aboutalebi 2019). Duan et al. (2023a) delved into the corrosion mechanisms of various coatings, from the conventional epoxy (EP) to EP formulations enriched with h-BN, BNNSs, or CeO<sub>2</sub>@BNNS (as shown in Figure 7). Their investigation revealed that basic EP coatings could not fully prevent corrosive media infiltration due to micropores. However, integrating fillers typically strengthens the coatings' physical barriers against corrosion, although issues like filler agglomeration and inconsistent distribution may still allow corrosion to breach these defenses.

Further, Haddadi et al. illustrated that cerium cations (Ce<sup>3+</sup>) encapsulated in MXene substantially enhance the

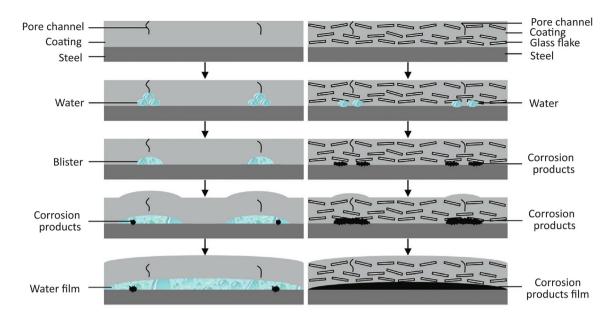


Figure 6: Schematic cross-sections of the failure process for coatings under high hydrostatic pressure (Liu et al. 2013a,b). Copyright 2013. Adapted with permission from Elsevier.

protective qualities of epoxy coatings on low-carbon steel (Haddadi et al. 2021). Similarly, Zhu et al. engineered a superhydrophobic CNTs-Cu hybrid/epoxy coating with selfcleaning capabilities for AH36 carbon steel. This coating retained its superhydrophobic properties after rigorous wear testing, demonstrating superior mechanical and corrosion resistance (Zhu et al. 2023a). Lastly, Gu et al. assessed the corrosion resistance of a graphene-based epoxy coating on low-carbon steel, discovering that a coating containing 0.5 wt% modified graphene outperformed the standard epoxy coating in corrosion resistance tests, effectively shielding the substrate from corrosion (Gu et al. 2015).

Meng et al. (2019) embarked on a comprehensive study to evaluate the efficacy of epoxy-based coatings augmented with graphene oxide (GO) and polyaniline (PANI) under the stress of alternating hydrostatic pressure (AHP). Modifying GO with PANI through an in-situ polymerization process

improved the coatings' corrosion resistance and mechanical strength. The key to this enhancement lies in the PANI's ability to more uniformly distribute GO sheets, thus reducing initial surface defects that could compromise the coating's integrity. Similarly, Ding et al. (2022) leveraged polydopamine as a novel reinforcing agent to improve graphene dispersion in epoxy coatings, resulting in the creation of bioinspired, multilayered graphene-epoxy composite coatings. Their approach led to a dramatic increase in the resistance of these composite coatings (Figure 8) – enhancing their performance by 2-3 orders of magnitude.

The curing process of epoxy coatings frequently results in micro-defect formation, detrimentally affecting the coatings' ability to protect against corrosion, leading to premature material degradation. In response, the scientific community has turned to nano-compounds with specialized functionalities as innovative additives to the epoxy resin.

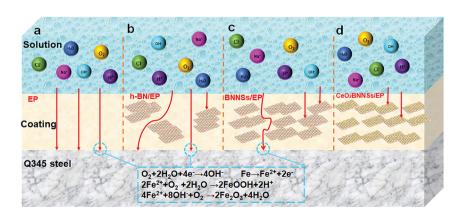


Figure 7: Schematic diagrams of the anticorrosive mechanisms of different coating systems (Duan et al. 2023a). Copyright 2023. Adapted with permission from John Wiley and Sons.

These nano-additives are meticulously engineered to fill the microscopic cracks and voids, consequently bolstering the mechanical integrity and overall efficacy of the coatings (Cui et al. 2021). Oiang et al. (2023) added GO-Ti<sub>3</sub>C<sub>2</sub>T<sub>v</sub> nanosheets to the epoxy resin. Through hydrostatic pressure soaking, salt spray technology and other tests, it was found that compared with the pure epoxy coating, the composite epoxy resin provided stronger physical barrier properties for the corrosion of Q235 steel (Figure 9a-c), which can effectively protect the steel. Shi et al. (2023) studied the corrosion resistance of aqueous epoxy resins with Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets functionalized with p-phenylenediamine (PPD) under-deep sea conditions. PPD-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> showed excellent dispersibility in epoxy resin, and effectively filled the inherent holes and defects in EP matrix. Prolonging the diffusion path of corroded substances in the coating is significant. PPD inhibitors were absorbed on the steel surface, reducing the formation of corrosion products, and the PPD-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> composite coating provided physical shielding and excellent active protection. Wu et al. explored the use of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> grafted with cellulose nanofibers (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@CNF) as nano-fillers, which markedly enhanced the epoxy coating's barrier properties and anti-corrosion performance (Wu et al. 2022). The oxygen-rich CNF improved the dispersion and compatibility between  $Ti_3C_2T_x$  and the epoxy resin, leading to a denser internal structure of the coating and

stronger adhesion to the metal substrate. Chen et al. crafted a novel silk fibroin- $Ti_3C_2T_x$  (SF- $Ti_3C_2T_x$ ) hybrid nanofiller, exhibiting exceptional compatibility with epoxy resin and being adept at remedying coating imperfections (Chen and Zhao 2021). This innovation greatly impedes the penetration of corrosive media, effectively prolonging the coating's lifespan and its corrosion resistance. Lastly, Ryu et al. investigated the impact of graphene oxide nanosheets' size on coating corrosion resistance (Figure 9d), finding that larger GO nanosheets resulted in better performance of the epoxy composite coating (Ryu et al. 2020).

In their comparative study of the anticorrosive properties of Cu-MOFS/OPA/EP and Zn-MOFS/OPA/EP coatings versus pure epoxy (EP), Wei et al. established that both coatings offer superior impedance in low-frequency regions, signifying enhanced blocking and shielding effects that boost the epoxy coatings' anticorrosive performance (Wei et al. 2022). Zhu et al. explored waterborne epoxy (WEP) nanocomposite coatings enriched with zinc oxide (ZnO), reduced graphene oxide (RGO), and polypyrrole (PPy). Their findings revealed that, relative to pure WEP coatings, the inclusion of nanomaterials significantly boosts corrosion resistance (Zhu et al. 2022). Notably, the WEP nanocomposite coating with a Z8R2P composition (mass ratio of ZnO:RGO: PPy = 8:2:1) showcased the highest impedance, the lowest corrosion current density, and the greatest charge transfer resistance

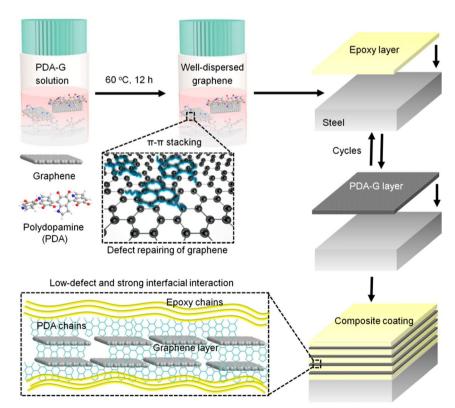


Figure 8: Schematic illustration of preparation process of layer-by-layer assembly I-PDA-G-EP composite coating. Copyright 2022. Adapted with permission from American Chemical Society.

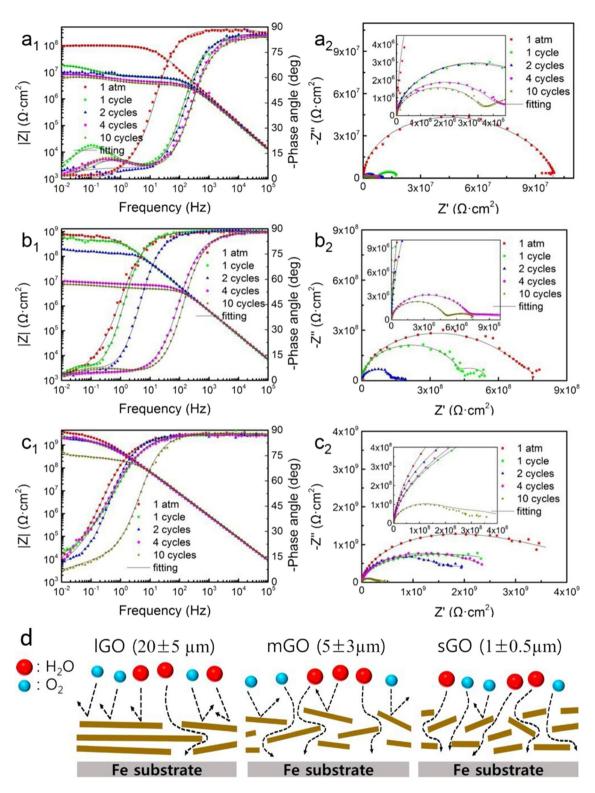


Figure 9: Bode diagrams and Nyquist plots for (a<sub>1</sub>, a<sub>2</sub>) pure EP, (b<sub>1</sub>, b<sub>2</sub>) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/EP, (c<sub>1</sub>, c<sub>2</sub>) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>@CNF/EP coatings at different immersion time under 15 MPa AHP environment (Wu et al. 2022). Copyright 2022. Adapted with permission from Elsevier. (d) Mechanism of the effect of GO size on the corrosion resistance of the Fe substrate (Ryu et al. 2020). Copyright 2020. Adapted with permission from Elsevier.

 $(R_{ct})$  at low frequencies, marking it as the most effective against corrosion. Li et al. discovered that adding appropriate amounts of nitrogen-doped carbon nanodots (CNDs) significantly reduces coating porosity and extends the diffusion path for corrosive agents, thereby enhancing the durability of epoxy coatings (Li et al. 2022). Furthermore, Deyab et al. found that epoxy coatings fortified with MgHP particles exhibit improved corrosion resistance and better mechanical properties (Devab et al. 2017).

Moreover, the addition of clay materials to epoxy resin markedly improves its anti-corrosion properties. Notably, sepiolite (SEP), recognized for its non-toxicity, environmental friendliness, and cost-effectiveness, enhances the passive anti-corrosion capabilities of coatings due to its unique lavered chain structure. Henriques et al. significantly boosted the corrosion resistance of epoxy coatings by modifying SEP with a phosphorus ionic liquid to serve as a filler, achieving a composite coating with an impedance vastly superior to that of pure epoxy (Henriques and Soares 2021). Chen et al. crafted an advanced epoxy coating that provides comprehensive active and passive corrosion protection by incorporating the corrosion inhibitor 2-mercaptobenzothiazole (MBT). This innovative coating exhibited exceptional anti-corrosion effectiveness, even under severe conditions (5 wt% NaCl and pH = 3) (Chen et al. 2022).

In a further innovation, Wei et al. combined a conventional epoxy protective coating with a super-duplex coating (Wei et al. 2020). Their immersion and salt spray tests demonstrated that this composite coating significantly reduces the penetration of water and various low-surface tension liquids, substantially improving the corrosion resistance of the underlying substrate.

In order to investigate further the role hydrostatic pressure and fluid flow play in the degradation of coatings under deep-sea environments, Meng et al. studied the corrosion resistance of an epoxy varnish coating/steel system under simulated deep-sea fluid pressure (FP) by physical property test, electrochemical measurement, and finite element model. It proposed the failure mechanism of the coating under hydrodynamic conditions (Meng et al. 2021). As shown in Figure 10, the fluid flow provides the initial kinetic energy for water, the hydrostatic pressure difference reduces the energy barrier of water absorption, and the internal stress of expansion is the cause of cracking, resulting in the rapid deterioration of the mechanical properties and protective properties of the coating under FP conditions.

In summary, the failure process of epoxy resin-based protective coatings can be summarised in three steps. The process begins with water penetrating the coating through pre-existing surface pores, a situation exacerbated by high

hydrostatic or varying pressures. This compromises the integrity of the coating/steel interface, leading to a marked decrease in adhesion. The ensuing stress further damages the pigment/adhesive bond, expanding the pores and further weakening the surface integrity. As water progresses through the coating/steel interface, it triggers extensive blistering and the development of corrosion sites beneath the coating. This progression of blistering and corrosion ultimately creates a continuous layer of water filled with corrosion by-products over the interface, signifying the coating's complete failure. This analysis highlights that rapid water movement through the coating and the adverse effects of pressure on the coating-metal system are the primary drivers of coating degradation (Tian et al. 2014).

#### 4.2 Aging failure of polyurethane-based coatings

Polyurethane (PU), a polymer composed of soft and hard segments, stands out among organic coatings for its exceptional chemical and wear resistance, toughness, and corrosion resistance. These coatings are frequently used as topcoats in electronics, aviation, and marine engineering sectors (Hou et al. 2018; Zhang et al. 2012). However, environmental factors like temperature, humidity, and corrosive agents can accelerate their aging, diminishing their protective capabilities over time. Ma et al. identified the hydrolysis of urethane bonds within the polyurethane chain as the primary cause of this degradation (Ma et al. 2023). Furthermore, Mirhosseini et al. highlighted that the polyol type significantly influences the wear resistance of polyurethane coatings, independently of the NCO/OH ratio (Mirhosseini et al. 2016). The bond strength between the coating and its substrate is vital for maintaining corrosion resistance. Modifying the polyurethane to enhance this adhesion can significantly improve its corrosion resistance (Kuang et al. 2021). In an exploration of how waterborne polyurethane varnish benefits from silane modification, Zhou et al. uncovered that nucleophilic addition and intramolecular rearrangement reactions between isocyanate (-NCO) and amino (-NH<sub>2</sub>) groups shift the bond from physical to chemical (Zhou et al. 2022b). This change dramatically enhances the adhesion to the substrate and boosts the initial protection performance. Research into the degradation of acrylic polyurethane coatings in high-humidity and saline environments indicates that photodegradation and powdering occur as initial signs of aging, likely due to the breaking of carbamate bonds (Ma et al. 2018; Zhang et al. 2020). This leads to a decrease in the coating's compactness and its overall protective capability.

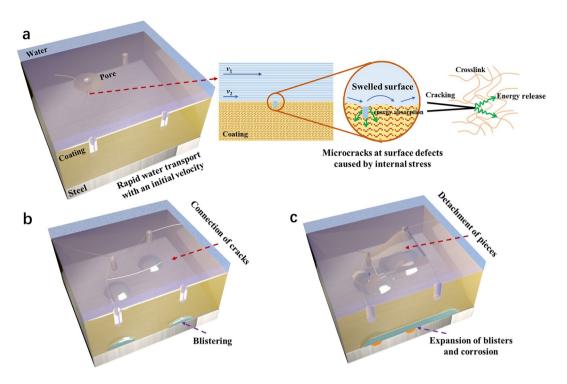
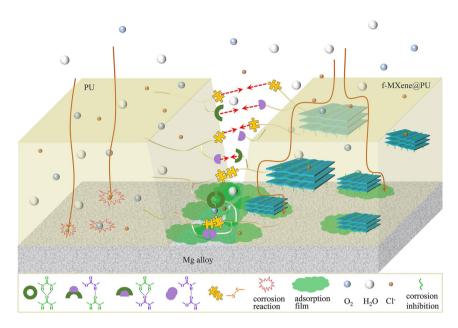


Figure 10: Schematic of the failure mechanism of coating under FP hydrodynamic condition (Meng et al. 2021). Copyright 2021. Adapted with permission from Elsevier.

Researchers have developed multiple strategies to improve the properties of polyurethanes, aiming to enhance the corrosion resistance of coatings in corrosive environments and extend the lifespan of substrates. These approaches have successfully enhanced the protective qualities of polymer coatings by integrating fillers, additives, and pigments (Haghdadeh et al. 2019; Li et al. 2023b; Meng et al. 2018). Wan Mohamad Kamaruzzaman et al. found that incorporating ES powder, a readily available and costeffective bio-waste, into polyurethane coatings led to increased corrosion resistance, with no cracks or pores detected after immersion in artificial seawater, especially at higher ES powder concentrations (Wan Mohamad Kamaruzzaman et al. 2022). In their investigation of a fluorinated polyurethane protective coating, Xu et al. discovered that accelerated aging tests improved corrosion resistance and mitigated corrosion spread after damage (Xu et al. 2022). Abil and Arefinia reported that adding talc particles to polyurethane coatings significantly boosted their corrosion resistance thanks to enhanced barrier properties, extended diffusion paths for corrosive agents, and stronger adhesion to metal substrates (Abil and Arefinia 2022). Li et al. demonstrated that adding just 0.2 wt% graphene to waterborne polyurethane markedly increased the coatings' corrosion resistance (Li et al. 2016). Additionally, Li et al. (2021a) achieved ultra-low friction and enhanced corrosion

resistance in composite coatings by incorporating terminated silicone oils (TSOs) into polyurethane resins, with the CH<sub>3</sub>-TSO variant notably increasing the PU coating surface's hydrophobicity and, consequently, its corrosion resistance. As shown in Figure 11, embedding Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> into polyurethane coatings also enhanced their corrosion resistance, further evidencing the effectiveness of these innovative modifications (Li et al. 2023b).

The incorporation of nanoscale materials significantly improves the anti-corrosion and mechanical properties of PU coatings. Rajitha et al. enhanced PU matrix anticorrosive properties by dispersing zinc oxide/reduced graphene oxide (ZnO/rGO) and zinc oxide/multi-walled carbon nanotubes (ZnO/MWCNT) nanohybrids, noting ZnO's role in effectively distributing rGO and CNTs (Rajitha et al. 2020). Cai et al. developed a nanocomposite reinforced PU coating using ultrasonically dispersed polydopamine-coated carbon nanotubes (PDA@CNTs) as nano-fillers, which improved the coatings' structural density and corrosion resistance due to the nanofillers' excellent dispersibility (Cai et al. 2018). Salazar-Bravo et al. observed that adding ZnO nanoparticles to commercial waterborne polyurethanes (WBPU) not only enhanced the barrier properties of WBPU but also provided active protection through the formation of zinc hydroxide at cathodic sites (Salazar-Bravo et al. 2019). Similarly, Ye et al. crafted a ZnO array/PU nanocomposite coating for stainless



**Figure 11:** Anti-corrosion/self-healing mechanism of f-MXene@PU coating (Li et al. 2023b). Copyright 2023. Adapted with permission from Elsevier.

steel, which markedly decreased the corrosion current following immersion in 3.5 % NaCl (Ye et al. 2019). This improvement in corrosion resistance was ascribed to the structural, electronic, and chemical influences of the ZnO arrays. Kumar et al. demonstrated that embedding SiO<sub>2</sub> nanoparticles in PU coatings increased the substrate's corrosion potential and decreased corrosion density, indicating improved composite coating corrosion resistance (Kumar and Meena 2021). Additionally, using Pd-ZrO<sub>2</sub> nanoparticles as a nanofiller has been shown to provide corrosion stability for coatings. Jothi et al. reduced the accessibility of corrosive ions to the mild steel surface by incorporating synthetic nanoparticles into PU coatings applied via compressed air spraying, thereby controlling corrosion by minimizing cracks and pores in the PU (Jothi et al. 2022).

In addition, the sol-gel coating acts as a passivation layer on the substrate. Yu et al. prepared organic-inorganic sol-gel reinforced waterborne polyurethane coatings in which the sol-gel system in the coating condensed to form an interpenetrating network (Yu and Tai 2021). The corrosion resistance of the reinforced PU coating was greatly improved, and compared with some commercial coatings, the layer had superior performance. It could effectively extend the service life of the substrate.

#### 4.3 Aging failure of acrylate-based coatings

Acrylic polymers (PAA) stand out for their exceptional water resistance, durability, adhesion, cost-effectiveness, environmental sustainability, and strong hydrogen bonding networks (Ji et al. 2021). Their formulation as waterborne products makes polyacrylate coatings increasingly popular for their eco-friendly qualities.

Feng et al. incorporated corrosion inhibitor-loaded microcapsules into these coatings to boost corrosion resistance (Feng et al. 2023). These capsules release inhibitors in response to pH fluctuations, providing secondary metal protection when the coating is compromised. Silva et al. enhanced a commercial acrylic coating with a binder composed of PANI-based emerald green imide and an inert plasticizer, crafting an intelligent coating that delivers anodic protection to carbon steel (Silva et al. 2020). Eduok et al. fortified acrylic resins with nano-zirconia (ZrO2NPs) for Q235 steel, showing that ZrO<sub>2</sub>NPs block corrosive media entry, thus safeguarding the steel (Eduok et al. 2019). The adaptable, functional structures of acrylic copolymers permit enhancements in corrosion resistance through strategic modifications. Zhou et al. combined acrylate copolymers with epoxy to produce composite coatings, significantly improving their density, adhesion, hydrophobicity, weather tolerance, and corrosion resistance, thanks to the copolymers' hydrogen bonding network (Zhou et al. 2022a). Meng et al. significantly enhanced the mechanical durability and anti-corrosion characteristics of water-based acrylic resins by using synergistic modifications with low surface energy substances, external crosslinkers, and anticorrosion fillers, yielding core-shell fluorosilica-acrylate resins (Meng et al. 2022). Thirumoolan et al. created copolymers of benzoylphenyl methacrylate and methoxyethyl methacrylate, demonstrating impressive protective efficiency against mild steel in corrosive settings (Thirumoolan et al. 2022). Li et al. leveraged phosphorylated graphene oxide and PedGO nanosheets as reinforcing agents in acrylate-epoxy emulsion coatings, thus improving the coatings' barrier properties against corrosive elements and boosting corrosion protection (Li et al. 2018). Xia et al. showed that vegetated titanium dioxide composites in polvacrylate coatings, as evidenced by Tafel curves, significantly contribute to metal corrosion protection through high photoelectric conversion efficiency (Xia et al. 2020b). Yang et al. incorporated graphite nanoparticles (f-GNPs) into acrylic resin to improve the corrosion resistance of the coating, thereby achieving better interface and dispersion effects and enhancing the Coulomb barrier effect (Yang et al. 2021). Finally, He et al. discovered that adding cellulose nanocrystals to aqueous acrylate matrix coatings markedly improves long-term corrosion resistance, facilitated by hydrogen bonding interactions between cellulose nanocrystals and the coatings (He et al. 2019).

#### 4.4 Aging failure of polyaniline coatings

Polyaniline (PANI), a semiconducting polymer consisting of benzo and quinone rings, is renowned for its conductive properties (Tanami et al. 2010). It is highly valued in the formulation of anticorrosive coatings and as a component in organic coatings, thanks to its notable electrochemical properties, corrosion resistance, and chemical stability (Chen et al. 2016; Cui et al. 2015; Ghorbani and Eisazadeh 2012; Liao et al. 2019).

Huang et al. augmented a PANI-based coating by integrating TiO<sub>2</sub> nanoparticles, known for their low surface energy. This addition not only heightened the coating's electrical conductivity but also resulted in a layered structure that formed a robust barrier, significantly enhancing the coating's ability to resist corrosion

(Huang et al. 2020). Shi et al. crafted a PANI/modified SiO<sub>2</sub> composite coating, with the modified SiO<sub>2</sub> effectively filling the voids in the electrostatically spun PANI layer, yielding a composite renowned for its exceptional corrosion resistance (Shi et al. 2017). Moreover, Hu et al. developed superhydrophobic and corrosion-resistant STA/PTC (SPTC)-Zn coatings and analyzed the corrosion mechanisms of four distinct samples (Hu et al. 2022), as depicted in Figure 12. Among these, the SPTC-Zn coatings demonstrated unparalleled corrosion resistance, an achievement credited to the PTC superhydrophobic layer's innovative use of PANI's redox potential to establish an enhanced protective passivation layer on zinc surfaces. This strategic approach effectively increased the diffusion pathways for corrosive agents, significantly boosting the coatings' protective capabilities.

Zhao et al. adeptly prepared PANI/PMMA (polyaniline/ poly(methyl methacrylate)) microfibers via an electrostatic spinning method, applying them as an anti-corrosion coating for carbon steel. Remarkably, the electrospun PANI/PMMA coating achieved an anti-corrosion efficiency of 99.99 % in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, nearly 500 times more effective than traditional drop-cast PANI/PMMA coatings (Zhao et al. 2016). Bandeira et al. revealed that a hybrid coating combining polyaniline (PANI) with polyvinyl chloride (PVC) offers superior corrosion protection for steel, leveraging both passivation and barrier mechanisms (Bandeira et al. 2017). Furthermore, Zhu et al. synthesized a highly electroactive polyaniline-polyaniline carbide composite through in-situ polymerization, intended as a filler for PVB coatings. Illustrated in Figure 13, this composite coating demonstrated optimal low-frequency impedance and the lowest corrosion rate across various corrosive settings, providing durable corrosion protection to the substrate for over 240 days (Zhu et al. 2023b).

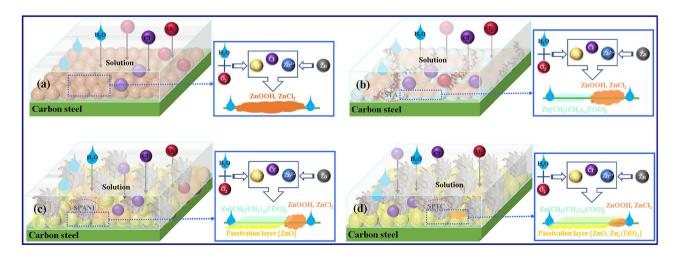


Figure 12: Interfacial models of the corrosion protection mechanism of (a) Zn, (b) STA-Zn, (c) SPANI-Zn, and (d) SPTC-Zn coatings immersed in 3.5 % NaCl solution, respectively (Hu et al. 2022). Copyright 2022. Adapted with permission from Elsevier.

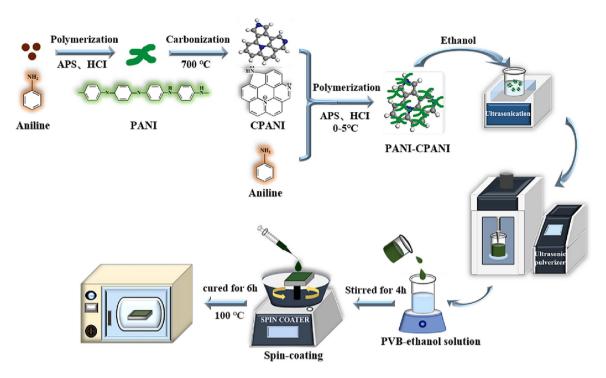


Figure 13: Schematic diagram of the preparation process (Zhu et al. 2023b). Copyright 2023. Adapted with permission from Elsevier.

#### 5 Conclusions

This study delves into the protection and failure mechanisms of service metals and polymer-metal systems within the demanding context of deep-sea environments. It scrutinizes the behavior of both metallic and non-metallic polymer materials when exposed to these conditions. The deep sea's unique characteristics notably elevate the risk of material degradation, where corrosion presents a critical challenge to metals deployed in such service roles. In response, a variety of corrosion prevention strategies have been devised, including the application of protective coatings, modifications to the metal substrate, and the employment of electrochemical protection techniques. Among these, protective coatings stand out as the most effective and straightforward approach, and are widely used in all kinds of Marine facilities and equipment surfaces, providing theoretical and technical support for deep-sea protection.

#### 6 Outlook

Although anti-corrosion coatings have benefitted from decades of dedicated research, most of these protective solutions remain under experimental investigation. Future efforts could focus on the following areas to advance our

understanding and application of these protective measures:

- (1) Material science advances: the wide range of raw materials for coatings, along with variations in their molecular weights and synthesis processes, underscores the absence of a universal solution. Considering the critical aspects of process routes, cost-effectiveness, and production scalability, it is essential to devise synthesis processes that are simpler, more economical, highly efficient, and broadly applicable.
- (2) Microstructural characterization: while current research primarily focuses on extending the lifespan of materials and tackling macroscopic failures, there is an increasing imperative to explore the molecular structure. This exploration is crucial for understanding the failure processes and mechanisms of metals and anticorrosion coatings at a microscopic level. Future research should aim to merge microstructural characterization with molecular correlation simulations, providing a deep dive into the fundamental failure mechanisms of these materials.
- (3) Real-sea condition testing: deep-sea corrosion testing is primarily limited to simulated laboratory environments, which significantly diverges from actual sea conditions. This divergence highlights the need for materials that meet the stringent demands of natural marine environments. Considering the challenges in generalizing

real-sea test results, future studies must integrate finite element analysis to narrow this gap. This approach opens up vast opportunities for improving the protective capabilities of materials against corrosion.

In addition to the previously mentioned coatings, such as epoxy resin, polyurethane, acrylate-based, and polyaniline, other noteworthy alternatives include asphalt coatings, epoxy-polyurethane composite coatings, and lacquer phenol anti-corrosion coatings. These coatings fulfill diverse protective roles, ranging from topcoats to intermediate coats and primers, each tailored to specific requirements.

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