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Review

Environmentally Friendly Anticorrosive Polymeric Coatings

Mirko Faccini [1,*], Lorenzo Bautista [2], Laura Soldi [2], Ana M. Escobar [2], Manuela Altavilla [1], Martí Calvet [2], Anna Domènech [2] and Eva Domínguez [2]

1 Centro de Excelencia en Nanotecnología (CEN), Leitat Chile, Calle Román Díaz 532, Providencia, Santiago 7500724, Chile; maltavilla@leitat.cl
2 Leitat Technological Center, Surface Chemistry Area, Applied Chemistry & Materials Department, Terrassa 08225, Barcelona, Spain; lbautista@leitat.org (L.B.); lsoldi@leitat.org (L.S.); amescobar@leitat.org (A.M.E.); mcalvet@leitat.org (M.C.); adomenech@leitat.org (A.D.); edominguez@leitat.org (E.D.)
* Correspondence: mfaccini@leitat.cl

Abstract: This paper provides a synthetic and comprehensive overview on environmentally friendly anticorrosive polymeric coatings. Firstly, the economic and environmental impact of corrosion is presented to highlight the need of anticorrosive polymeric coatings as a flexible and effective solution to protect a metal. Secondly, the implementation of regulations together with the consumer awareness for environmental considerations and protection of health are the driving force for a progressive but significant change in the sector. Therefore, within the protective organic coatings market, this article provides a review of the most recent developments in environmentally friendly solutions, including bio-based and water-borne epoxy, hyperbranched polyester for low- volatile organic compounds (VOC) coatings, waterborne polyurethane and non-isocyanate polyurethanes (NIPUs), and graphene or bio-based fillers for acrylics. Moreover, this paper outlines new trends such as smart additives, bio-based corrosion inhibitors, and functional antibiocorrosive coatings as superhydrophobics. Finally, industrially relevant applications of environmentally friendly anticorrosive polymeric coatings including solutions for marine and off-shore industries are summarized.

Keywords: polymeric coatings; anticorrosive; environmentally friendly; protective coating; bio-based; waterborne; low VOC

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1. Introduction

Corrosion Cost and Environmental Impact

Corrosion is a universal topic, for many accepted as an inevitable process. The penalties of failures from corrosion are highly impactful from a human safety perspective and an economic point of view, including safety hazards or plant interruptions.

The conclusion of significant studies undertaken by several countries was that corrosion represents a constant charge to the nation's gross national product (GDP). The National Association of Corrosion Engineers (NACE International) studied the role of corrosion management in industry and government impact in the US and estimated a global cost of corrosion of US $2.5 trillion, equivalent to 3.4% of US GDP, and from approximately 1 to 5 percent of GDP of each nation. These numbers are considered to be conservative since only well-documented costs can be used for study: corrosion control management as well as maintenance costs, monitoring, inspection and fewer failures are difficult to measure. Nevertheless, it was observed that indirect costs due to corrosion damage are often significantly greater than direct costs. Hence, the total cost which should include direct plus indirect cost could double the corrosion cost up to six percent of US GDP [1,2].

Health hazards and environmental impact of corroded materials, which could be considered as indirect costs, have been widely studied. Especially, the runoff of multiple metal ions (iron, zinc, lead, manganese) causing the contamination of the surrounding environment and drinking water systems were reported [3–7]. Moreover, the iron rust influence on the growth rate of Legionella bacteria [8], chemical emissions from cathodic protection of offshore wind farms (OWF) [9], or the environmental impact of rust removal techniques are other examples of environmental concerns [10].

Anticorrosive polymeric coatings have gained high potential and flexibility against metal protection compared to non-polymeric ones, as they can be designed and formulated to achieve more than one protective mechanism. This review is focused on anticorrosive polymeric coatings, paying special attention on environmentally friendly solutions able to achieve a proper balance between cost, technical performance, and environmental issues.

Therefore, the need to overcome the economic damages generated by corrosion phenomena has been faced through the development of several coating technologies. This review is focused on anticorrosive polymeric coatings as a flexible and effective solution against corrosion by means of different and simultaneous mechanisms of corrosion inhibition. A comprehensive vision of the topic is provided, together with a state of the art for eco-friendly polymeric coatings organized in four main categories, according to the polymer resin type: epoxy, polyester, polyurethane, and acrylic.

Above all, the present work aims to give an overall picture on how the coating market is evolving as a response to the public, government, and consumers' commitment to sustainability. Special attention is paid to new trends in the anticorrosive coating field, as the scientific community is addressing the high demand for environmentally friendly coatings with innovative solutions. Moreover, a selection of applications is made to highlight the urgency of a proper balance between cost, technical performance, and environmental issues in the coating sector.

2. Anticorrosive Coating Market and Its Challenges

Corrosion affects countless industries. One of the most significant success stories in corrosion control is the change in corrosion management strategy and application of innovative technology in the automotive industry, as highlighted by NACE's report [11]. Before 1975, car manufacturers used minimal protective solutions and corrosion was costing the industry billions of US$ annually. Since 1975, corrosion management solutions started to be implemented by car manufacturers, leading to an annual savings in 1999 compared to 1975 of 9.6 billion US$ or 52% in corrosion-related manufacturing and operation costs of vehicles. As result, cost of corrosion per unit of new vehicle decreased by 44% in 1999 compared to 1975 (Figure 1).

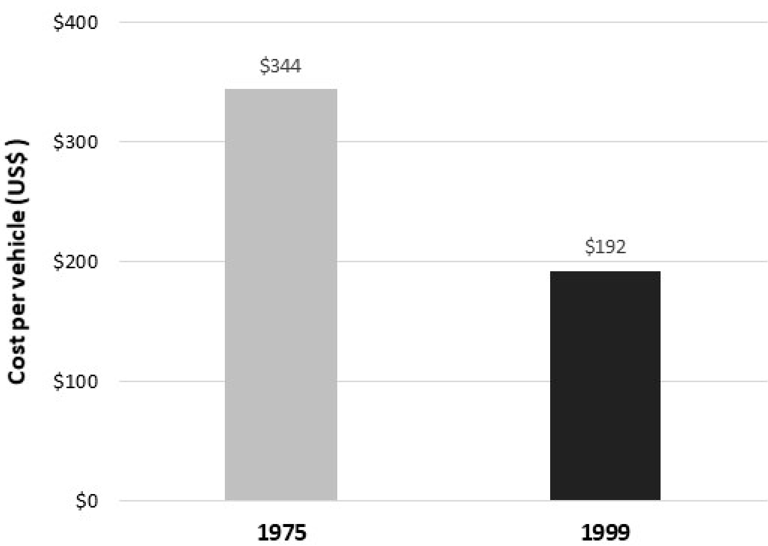

Figure 1. Corrosion-related costs on new vehicle manufacturing in 1999 compared to 1975. Numbers are adjusted for inflation.

Corrosion protection coatings are applied on a wide range of surfaces to guarantee the function and integrity of the part from damage due to the environment. The global protective coating market was valued in 2018 at EUR 26.5 billion. The research made by the IRL group estimated 7.4 million tons in volume in 2018, with growth expectations of more than 2 million tons by 2023 [12,13]. The region that will be responsible for the major volume increase is Asia-Pacific, with the largest consumption of these coatings systems, representing 84% of the total global volume (6.2 million metric tons) in 2018. In terms of consumption, the American continent consumed 0.5 million tons (7% of the total global volume) last year, and Europe 0.4 million tons. According to the IRL group and the European Council of the Paint, Printing Ink, and Artist's Colours Industry (CEPE), a slight growth is expected for both markets in 2023 (Figure 2).

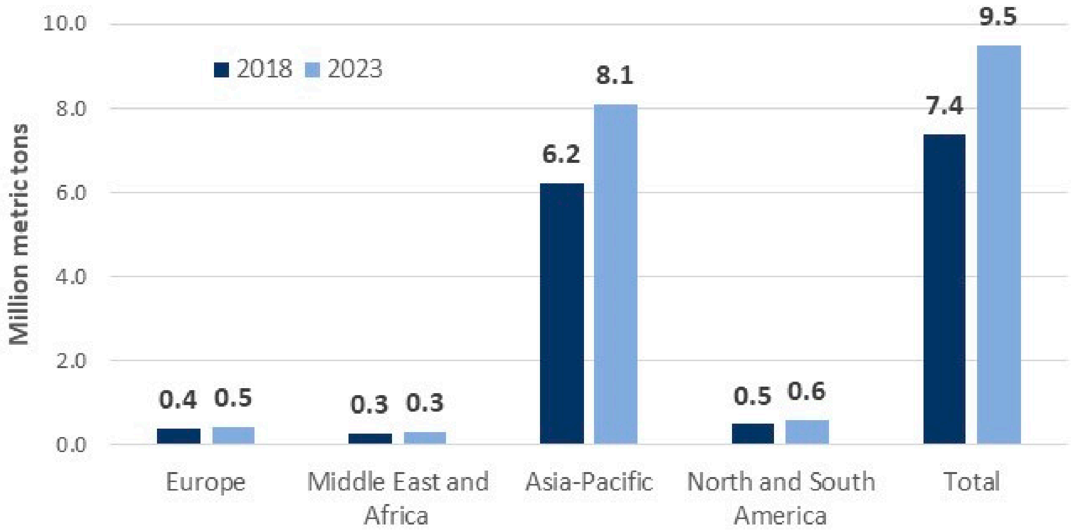

Figure 2. Metric tons of corrosion protection materials consumed by region in 2018 and expected growth in 2023.

The demand is highly related with public expenditure on infrastructure and the growth of the increasing demand from power generation, but also automotive and transport, and oil and gas sectors. Therefore, global paints and coating markets is expected to have a Compound Annual Growth Rate (CAGR) of 8.5% from 2020 to 2021. Nevertheless, due to the outbreak of COVID-19, predictions of CAGR now reach 4% for 2025 because of companies rearranging operations, such as remote working or closure of commercial activities that resulted in operational changes [14–16].

The cost of coating materials for a maintenance overhaul ranges between 5 to 21% of the total costs while surface preparation accounts for about 45% of the total. Although spending on high-performance anticorrosive coatings systems, such as high performance epoxy polyamide, urethane or zinc-rich systems, may look expensive, it may make savings of nearly 40% when service life is greater than 10 years [2].

Organic coatings are the most widely used coatings for corrosion protection of metallic materials especially in transport (e.g., automobiles, aircraft, ships, etc.) and infrastructure sector (e.g., pipelines, bridges, buildings, etc.) [17]. However, it is worth mentioning non-polymeric anticorrosive solutions that have a major industrial role like: phosphates [18], chromates [19], silicates [20], and metallic coatings (anodizing, galvanized, electroplating, thermal spray, cladding) [21–23]. While on one hand they show outstanding anticorrosive properties, on the other hand they need to be replaced with more environmentally friendly technologies (no generation of sludge, avoid the use of toxic substance, etc.). For example, the elimination of hexavalent chromium and heavy metals in general (lead, mercury) from coating formulation and coating processes is still an important topic for the anticorrosive coating sector and especially for the aerospace industry [24]. Therefore, the industry and academic entities have focused their effort in the development of inorganic coatings based on sol-gel technologies and hybrid inorganic-organic pre-treatments such as nano ceramic coatings using titanium [25], zirconium [26], silicate, rare earth metals [27], and molybdates [28] compounds as greener alternatives. These inorganic coatings are generally prepared in highly diluted solutions, which means employing large volumes of water. Hence, the resulting residual water requires to be post-treated before discharge to comply with emission limit values for metals and other pollutants set by the Environmental Quality Standards. These legal limits are established to minimize the environmental impact and especially to protect aquatic life [29].

However, the anticorrosive coating market is dominated by organic coating which is generally divided in segments based on the type of resin or binder: epoxy, polyurethane, acrylic, alkyd, or polyester. Most of the organic coatings are applied in liquid form and therefore the organic solvents are one of the main components of the coating formulation. The European community recently started looking into controlling or limiting the emission of volatile organic compounds (VOC), leveraging the need to develop new VOC compliant products, with low amount of organic solvent [30]. To solve this challenge, several potential solutions were identified, including high-solid coating [31], waterborne [32], and ultra-violet (UV) light-cured coatings [33]. The replacement of hazardous materials, such as isocyanate to produce polyurethane is still an important challenge for the coating sector due to its consequence on human health. In fact, the main effects of hazardous exposures to isocyanate are occupational asthma and other lung problems, as well as irritation of the eyes, nose, throat, and skin [34]. The implementation of REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) regulation, the stringent regulations imposed by government and the rise in consumer awareness for green and more sustainable solutions drive the anticorrosive coating market to environmentally friendly polymeric coatings. Furthermore, the development of bio-based raw materials for coatings such as resin [35], solvent [36], and additives [37] is becoming the focus of attention for substituting fossil ones. However, the availability of raw materials and the cost of environmentally friendly coating are still two major constrains for the growth of this market.

3. Protective Mechanism of Anticorrosive Coatings

Anticorrosive coatings are generally classified in accordance with the mechanisms by which they protect a metal against corrosion. Each form of corrosion may differ between systems, environment, material design and engineering, and other variables [38–40]. Typically, a protective coating is composed by several layers where the primer is in direct contact with the metal, the intermediate coats are located in between, and the topcoat is exposed to the external environment. The three basic protective mechanisms of anticorrosive coatings are [41]:

i. Barrier coatings or impermeable coatings: They act by blocking the transport of aggressive species into the surface such as water, gases (i.e., CO_2, SO_2 in industrial atmosphere), ions (Cl^- in marine atmosphere), or electrons. This can be obtained by a chemical conversion layer, or by addition of pigments to the coating. This type of coating may be used as primer, intermediate, or topcoat, and are often applied on immersed structures.

ii. Inhibitive coatings: In contrast with coatings based on impermeability, inhibitive coatings avoid corrosion by reacting with the environment to provide a protective film or barrier on the metallic surface. The inhibitive pigments are generally inorganic salts, which are slightly water soluble. This type of coating is primarily applied as primer because they are solely effective if dissolved constituents can react with the metal. They are mainly applied in industrial environment when the risk of atmospheric corrosion is high and are generally not recommended for immersion in water or burial in soil.

iii. Sacrificial coatings: They rely on the principle of galvanic corrosion for the protection of metals against corrosion. The substrate is coated by a metal or an alloy that is electrochemically more active than the substrate itself. Coatings formulated with metallic zinc powder are extensively employed for corrosion protection of steel structures. This type of coatings is only applied as primers because they need an electrical contact between the substrate and the sacrificial metal to be effective.

4. Developments in Environmentally Friendly Polymeric Coatings

The binder can be considered the most important component of an anticorrosive coating [42]. In fact, the appearance and anticorrosive properties of a dry organic coating depend on the chemical composition and the curing mechanism of the binder. Therefore, in this review the coatings system will be divided into four main categories based on the resin type: epoxy, polyester, polyurethane, and acrylic.

4.1. Epoxy

Epoxy resins have been used in many high performance coatings [41] due to their high chemical stability, resistance to heat, water, and excellent adhesion to metals. They are obtained by a condensation reaction between diphenyl propane derivatives and epichlorohydrin in the presence of a basic catalyst. The most used diphenyl propane to prepare solvent-borne epoxy resins is bisphenol A (BPA). Bisphenol A can be replaced with glycerol or other aliphatic polyols in the preparation of epoxy resins. Several synthetic pathways [43] led to the production of different epoxy resins: cycloaliphatic, trifunctional, tetrafunctional, Novolac, containing F, P, Si, and most of the recent bio-based ones. The final application of the epoxy resin is the key factor for the selection of the type of resins and curing system used in the coating formulation. For example, Epoxy Novolac, that presents high cross-linking properties, is a good choice for extremely aggressive environments. The molecular weight of the epoxy resin determines a wide range of the coating's properties such as viscosity, flexibility, hardness, solvent resistance, adhesion, and substrate wetting. Higher molecular weight epoxy resins contain many free hydroxyl groups that can generate cross-linking reactions with acids and isocyanates or can be esterified with fatty acids. Traditionally, the curing system is based on amines, polyamines, amides, anhydrides by cationic polymerization, and by applying heat or photo-irradiation.

The production of bio-based epoxy resins [44] is gaining special attention starting from vegetables oils, such us soybean oil (ESO) and castor oil (ECO), that contain unsaturated groups and can easily undergo oxidation or epoxidation reactions. Baroncini at al [45] covered in a recent review the development of epoxy resins and curing agents from renewable resources underlying, among others, some potential applications for protective coatings.

The water-borne epoxy coating technology is based on liquid epoxy resin or on solid epoxy dispersion (2k-component) [46,47]. The main advantages of this technology are a low content of organic solvent, excellent adhesion with the intermediate coat and substrates. The performance of water-borne epoxy as protective coatings is still insufficient if compared to the solvent-borne in terms of chemical resistance, risk of flash rust, slow evaporation of water, and limited gloss stability. Moreover, there are already examples of successful applications of electrodeposition [48] of epoxy primer emulsions, which brings enormous advantages to the automotive industry and original equipment manufacturers (OEMs) [49,50]. Another approach is to apply zinc-rich epoxy coatings in order to achieve protection of metal substrates in highly aggressive environments such as the marine atmosphere [51]. The zinc reactivity with water is controlled by encapsulation using highly reactive amine-based hydrophobic polymers. Once the amines react with the epoxy, the zinc is again available as a sacrificial electrolytic anode to protect the iron substrates [52]. Wang at al [53] focused their study on epoxy silicate modified emulsions with high zinc powder content. The introduction of different percentages of epoxy into the silicate emulsion resulted in coatings formulations with improved impedance, lower water absorption, and better insulating effect compared to silicate emulsions.

An alternative to reduce the emission of organic solvents is to increase the solid content of solvent-based systems or to maximize the reduction of solvent content without losing film properties. One common strategy is using HAP (hazardous air pollutants) exempt solvents [54] and reactive diluents that have the properties to reduce the viscosity and to cross-link while being part of the cured network. Within this last concept, the inorganic-organic hybrids have been extensively studied for their anticorrosive properties. The latest findings by Chen et al. [55] outline that silicone-epoxy-silica coatings, obtained with an in-situ polymerization using tetraethoxysilane (TEOS) without a coupling agent, can be used as high solid coating with improved anticorrosion performance.

Finally, the possibility to formulate UV-curable corrosion protection coatings is still in progress due to the numerous challenges in the development of such a formulation. In particular, the cationic photoinduced process presents some advantages compared to the radical one due to the lack of inhibition by oxygen, lower shrinkage, and good mechanical and adhesion properties to various substrates [56]. Most recently, a summary of the progress in the field of cationic UV curing process was reported, underlining the synthesis of new photo initiators and the activation of frontal polymerization for the curing of thick systems [57]. An innovative dual curing coating was described by Ni et al. using a UV photoacid generator to simultaneously induce the sol-gel process and the cationic ring opening of diepoxy monomers [58]. This technology is a good example of a chromate-free approach for a primer and has potential to be applied as a coating in the aerospace industry.

4.2. Polyester

Base polyesters have been modified in several ways to obtain resin structures. Particularly important are hyperbranched/dendritic polymers as polyester due to their extraordinary properties as promising resins for both development of low-VOC coatings [59] and protection against severe corrosive environments [60]. Modification of a hyperbranched hydroxy-functional polyester to a thermoset resin structure is readily achieved via catalyzed esterification of the hydroxyl end-groups with acid chlorides or suitable anhydrides [61]. Different resins can be obtained depending on the type of the end-groups and structure and source of fatty acids or triglyceride oil, as can be seen in Figure 3. Some bio-based monomers have been proposed for substituting not renewable diacid parts. Hadzich et al. [62] developed a Sacha inchi oil-based alkyd resin. Results showed that the addition of penterythritol and Sacha inchi oil promoted an increase of anticorrosion behavior and outstanding adhesion properties in harsh conditions.

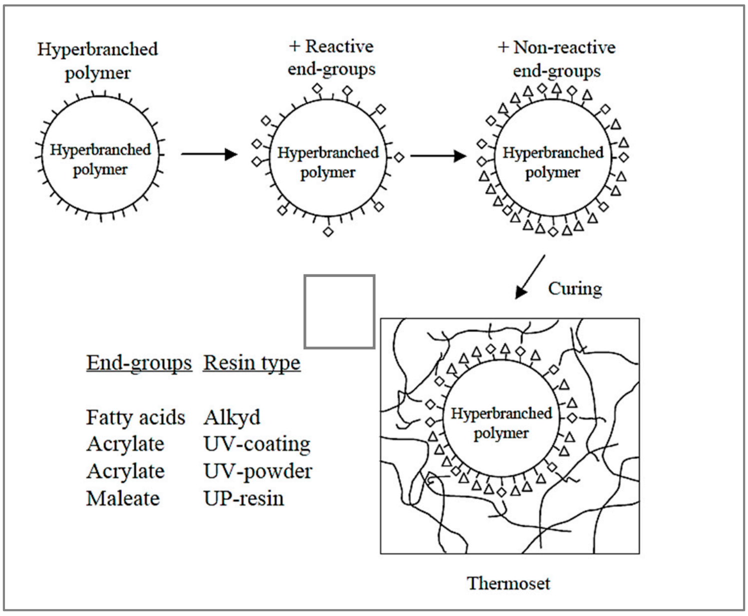

Figure 3. Principle of synthesis routes for different resin architectures based on hyperbranched polymers [61].

The application and curing process can emit toxic VOC from solvent-based coatings. This has resulted in a gradual shift from solvent borne coatings to waterborne coating minimizing VOC, other solutions are UV-curable coatings and high solid coatings. Alkyd resins based on glycolyzed PET waste and different aliphatic hyperbranched polyesters with fatty acid were developed by Ikladious et al. [63] in order to produce low-VOC coatings and to recycle PET materials. Hakeim et al. [64] reported the encapsulation of pigments with UV-curable hyperbranched polyester acrylate to improve printing performance and durability.

4.3. Polyurethane

Polyurethane (PU) coatings are organic polymers that are made through chemical reactions between a monoglyceride with a polyol and a diisocyanate to form a urethane oil or urethane alkyd. PU-based mixtures give a superior anticorrosive coating compared to ordinary alkyds resins [65,66]; however their synthesis is based on petroleum derivates. The development of waterborne PU is the first step to produce coating systems that are free of volatile solvent, non-polluting, and safe. Furthermore, waterborne PU have excellent physical, mechanical properties, and anticorrosion behavior. The development of greener chemical routes to substitute diols and diisocyanate petroleum-based materials is a challenge. For this reason, vegetable oils and fats are studied to synthesize polymers from renewable natural resources. They contain esters and carbon double bonds that can be functionalized to produce polyols, giving rise to bio-based PUs. The latest research focused on the development of coatings with polyether polyol and polyester polyol as raw materials and water-dispersible isocyanates as curing agent [67,68]. Marathe at al [69] combined the addition of natural polyol and polyester from neem oil with quinoline as corrosion inhibitors. The encapsulation of quinoline into a micro-reservoir allowed to overcome disadvantages caused by its direct addition into a coating layer.

Another sustainable feedstock for polyurethane coatings is functional soybean oil-based polyols [70]. Alagi et al. [71] studied this raw material combined with silane, ethylene oxide, and fluorine functionalization. The robust hydrophobic nature of silane-polyol-based PU coating promotes the characteristic anticorrosion behavior of the final coating. One of the most promising routes is the step-growth polyaddition of diamines with dicyclocarbonates leading to non-isocyanate polyurethanes (NIPUs). Doley et al. [72] investigated different chemical variables in order to obtain NIPUs with an improved thermal stability solvent-free/catalyst-free and bio-based content. Their NIPUs were produced by the reaction between epoxidized sunflower oil with CO_2 using tetrabutylammonium bromide (TBABr) as a catalyst.

Another strategy followed by researchers is the introduction of nanofillers of carbon to improve the barrier properties of protective coatings, thus enhancing their anticorrosion properties. The addition of graphene and its derivatives as reinforcement has been approached by different authors [73–75]. Li et al. [73] focused their study on the fabrication of well-dispersed graphene reinforced waterborne PU composite coatings, highlighting the critical factors affecting the barrier properties, as schematically illustrated in Figure 4. The superior anticorrosive behavior of the graphene-reinforced PU coatings can be attributed to their ability to form a network in the PU matrix that avoids the permeation of foreign molecules.

Carbon nanomaterials from Eucalyptus globulus leaves were produced by an eco-friendly process in order to strengthen a castor oil-based PU coating by Siyanbola et al. [76]. Their results showed great anticorrosion properties with 2% of carbonized coal ash of Eucalyptus globulus leaves. Hou et al. developed a novel waterborne PU coating with excellent anticorrosion properties by addition of just 2 wt% of multiwall carbon nanotubes (MCNT) as filler [77]. The MCNT act as barrier, increasing the diffusion path tortuosity for the permeating corrosive electrolyte, as schematically shown in Figure 5.

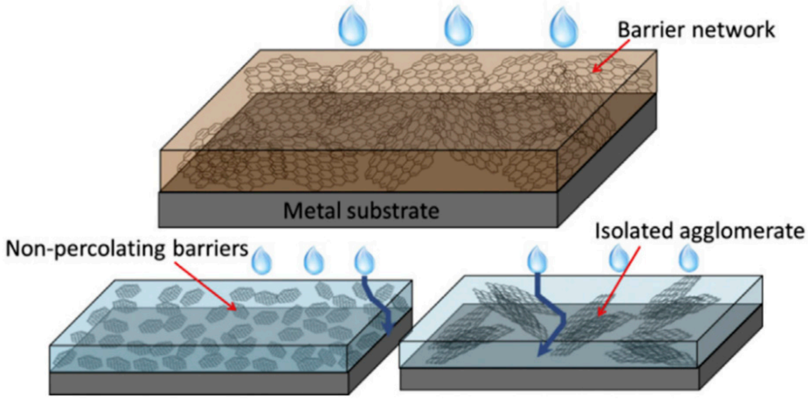

Figure 4. Schematics of the critical factors on the barrier properties of graphene reinforced polyurethane (PU) composite coatings [73].

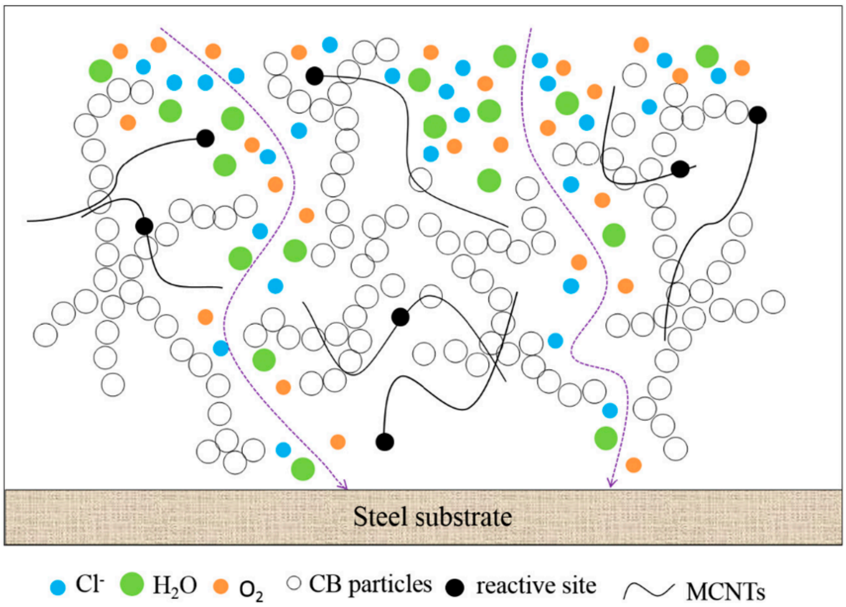

Figure 5. Schematic diagram of the proposed mechanism for nanocomposite PU coating exposed to 3.5% NaCl solution at pH = 7 [77].

Nanocrystalline cellulose is another eco-friendly reinforcing additive for improving the corrosion and mechanical resistance of PU coatings [78]. Finally, the anticorrosive behavior of NIPUs can be increased by the addition of fillers as ZnO nanoparticles. This solution is used in cathodic anticorrosive coatings; however, the high surface energy and the large surface area of ZnO particles make them prone to aggregate. To overcome this problem, Kathalewar et al. [79] studied different surface treatments of ZnO particles using silane compounds, demonstrating an increase of the anticorrosive property of the coating.

4.4. Acrylic

Acrylic paints are water-based coatings and, therefore, they are more environmentally friendly than classical epoxy or PU coatings. However, a dense cross-linking of waterborne acrylic coating is difficult to form, seriously limiting its durability and anticorrosion behavior. To overcome this drawback, researchers have focused their attempts on modifying the polymer coating by the addition of inorganic or organic materials.

Two-dimensional materials can be embedded into acrylic coatings to greatly improve the corrosion resistance of the resulting composite coatings due to their stable chemical and physical properties and unique morphology. The most common two-dimensional materials are graphene and graphene-like materials such as molybdenum disulphide (MoS_2). Gao et al. [80] introduced MoS_2 nanosheets into an acrylic emulsion, forming a three-dimensional network structure with chemical cross-linking points. The addition of MoS_2 sheets to the coating promotes an inhibition of the corrosive medium transmission and a reduction of the coating hydrophobicity. Carbon nanotubes (CNT) are another reinforcing agent for acrylic coatings because the presence of CNT reduces the through-porosity. The water diffusion and absorption in the CNT/acrylic coating are slower than those of the native acrylic coating, as Song et al. explained in their work [81].

Pure acrylic coatings have the tendency to result in surfaces with lots of micropore defects, which may be formed during the drying process. Li et al. [82] demonstrated that adding graphene-modified CeO_2 nanoflake in waterborne acrylic coating promotes a reduction of the amount of micropores and an increase of the anticorrosion performance of the final paint. This is due to the combination of the excellent barrier stability of graphene and the good corrosion inhibition of CeO_2, which can inhibit corrosion by releasing Ce^{3+}. The mechanism proposed by the authors is shown in Figure 6.

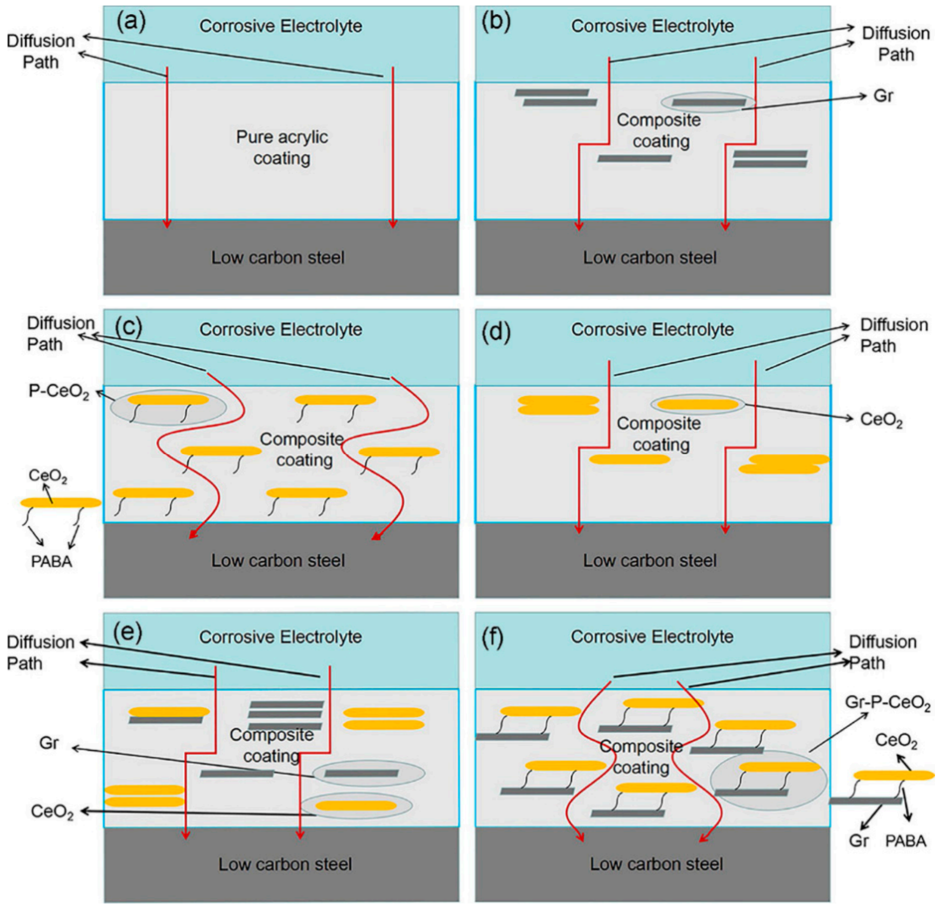

Figure 6. Schematic representation of corrosion mechanism by Gr-P-CeO_2 coatings with different barriers on mild steel substrate: (**a**) no barrier, (**b**) Gr (graphene), (**c**) CeO_2 nanoflakes modified with PABA (p-aminobenzoic acid), (**d**) CeO_2 nanoflakes unmodified, (**e**) Gr-CeO_2, the agglomeration between CeO_2 and Gr has reduced the corrosion resistance, (**f**) the best anticorrosion ability because it used PABA to link Gr and CeO_2 together by chemical bonding, which enhances the dispersion of the fillers in the coating [82].

Moreover, Rajkumar et al. [83] used silica nanoparticles obtained from rice husk following an eco-friendly process as efficient filler for acrylic anticorrosive coatings.

Organic-inorganic hybrids coatings, consisting of poly (methyl methacrylate) (PMMA), provide highly efficient anticorrosion coatings, especially when PMMA is covalently bonded to cerium nanoparticles, as studied by Harb et al. [84]. The electrochemical characterization of the resulting hybrid coatings showed a significant improvement in the anticorrosion properties, showing an impedance modulus 8 orders of magnitude higher than the bare carbon steel after 6 months of exposure to a saline solution [78,79].

The use of green corrosion inhibitors is also a potential pathway for the introduction of more environmentally friendly acrylic coatings into the market. The aqueous extract of the henna leaves is under investigation as a corrosion inhibitor for carbon steel, nickel, and zinc in alkaline, neutral, and acidic solutions. Zulkifli et al. [85] evaluated the anticorrosion behavior of henna leaves extract incorporated in an acrylic resin in order to protect aluminum alloy 5083 from corrosion. The formation of conducting pathways that reduce the protection ability was observed. More research focused on green approaches for polymeric coatings is needed.

5. New Trends

The urgency and necessity to reduce or eliminate VOC in anticorrosive coating formulations has gained increased attention in the last 15–20 years, leading to the three main solutions: water borne, high solid, and UV-curable coatings. These technologies are still being investigated to develop new or improved anticorrosive coating products. However, a huge quantity of low VOC or VOC-free coatings are currently commercially available and are still demanded by the market. New developments are generally improvements of previous products; therefore, they can be considered mature coating technologies.

On the contrary, several innovative technologies in the field of environmentally friendly polymeric coatings aimed to fight corrosion of parts or items have recently been identified as new trends. These novel technologies have been summarized in five different groups: smart additives, hyperbranched/hybrid polymer technologies, green corrosion inhibitors, bio-based materials, and superhydrophobic coatings, as depicted in Figure 7.

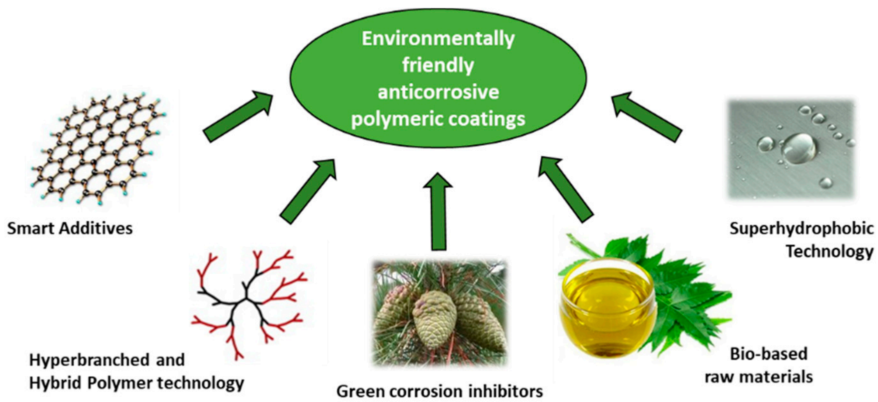

Figure 7. Schematic representation of new trends in the protective coating fields aiming for environmentally friendly solutions.

The use of smart additives to enhance properties of an anticorrosive coating is a new trend under development. In particular, the use of graphene is attractive due to its excellent anticorrosion properties, in fact graphene acts as a "barrier" in the coating, hindering the penetration of the corrosive species and creating a channel of electron flow between the sacrificial anode and the substrate in the coating [86]. For these characteristics, graphene has been added to Zn-rich epoxy coatings, achieving superior corrosion protection and reducing the zinc content in the epoxy primer formulation [87]. Moreover, smart additives such as micro-capsules of environmentally friendly molecules (e.g., lawsone) [88] and zeolites [89] were shown to impart self-curing properties to epoxy resins.

Most recently, hyperbranched polymers were used to formulate chemical resistant and low solvent durable coatings, thanks to their good properties such as high crosslinking density, good solubility, and high reactivity. Wang at al [90] applied a water borne hyperbranched acrylic polymer grafted onto SiO_2/TiO_2 composites on steel as a novel coating that passed 1000 h of salt spray test.

The use of plant extracts as green corrosion inhibitors has also attracted the attention of the scientific community. As an example, polyphenols extracted from different vegetable sources were employed to enhance the anticorrosive properties of coatings, showing promising results [91–93]. Montoya et al. [94] reported the development of an environmentally friendly epoxy primer using *Pinus Radiata* tannins extracted from the waste generated by the timber and paper industries. The coating showed an anticorrosive performance comparable to industrial solutions. The inhibitory activity of the extract is attributed to its high antioxidant power, which enables the formation of complexes with the metal surface, creating a protective layer that is impermeable to external agents. An environmentally friendly coating based on the natural product shellac was recently investigated [95]. A significant enhancement in the anticorrosive performance of copper substrates was achieved using aliphatic hydrophobic diamine as a crosslinking agent for modifying shellac structure and ethanol as a solvent. Another relevant example of successful application of bio-based raw material in anticorrosive coatings was the work of Zheng et al. [96]. The manuscript described the use of a diol named isorbide, which is obtained from glucose at a low cost, as reactant with 3-glycidylopropyltrimethixysilane to obtain a bio-based epoxy. The coating formulated with the addition of silica nanoparticles and a hydrophobic curing agent improves the corrosion protection. This coating has water-repellent properties as well with a contact angle around 142°. In fact, superhydrophobic properties enhance the barrier effect of coatings by increasing the repellency towards water and electrolytes.

Superhydrophobic polymeric coatings can be prepared by the introduction of low surface energy functionalities in the coating matrix, as well as nanomaterials in order to increase the surface roughness, mimicking the lotus effect [96,97]. Superhydrophobicity is also relevant for antifouling, anti-icing, and biocorrosion protection [97], which make these coatings interesting for applications where multifunctionality is required. For all these reasons, superhydrophobic coatings can be considered as a very promising strategy to achieve eco-friendly anticorrosive solutions.

6. Applications

According to ISO 12944-2:2017, the corrosive environments for steel structures are classified in three different categories, being: (i) atmospheric corrosion, (ii) immersed in water, and (iii) buried in soil. The corrosion stress of each environment is unique and generates different corrosion rates. This aspect indirectly determines the type of protective coating system needed for each category. The severity of the corrosion is classified according to its corrosion degree. In atmospheric environment, this scale goes from C1, which defines a very low corrosion level, to C5, for a very high level, and finally to CX for extremely corrosive environments. Table 1 summarizes the class definition together with the identification of the type of steel structures or applications that need a protective coating. The applications of anticorrosive coatings for class C1 and atmospheric environment are basically in heated buildings with clean atmospheres. Following the same rational, the class C2 is correlated with a low level of corrosion, which is usually found in metallic structures with a low level of pollution and unheated buildings where condensation may occur.

The main applications of anticorrosive coatings immersed in water are found in river installation (e.g., hydroelectric power plants) for fresh water (Im1); and harbor areas with metallic structures like sluice gates, locks, jetties; and offshore structures for sea (or brackish) water environments (Im2). Antifouling paints are usually applied onto anticorrosive protective coatings in several immersed applications such as fuel-saving antifouling coatings for ships and net cages used in the aquaculture industry [98]. Finally, the main applications in soil environment are found in buried tanks, steel piles, and steel pipes (Im3); and those immersed assets with cathodic protection (Im4). Suitable anticorrosive coating solutions can be designed for any specific application.

Table 1. Classification of corrosive environments for steel structures according to ISO 12944-2:2017.

Class Definition	Type of Structure That Needs an Anticorrosive Coating
C1, very low	Offices, shops, schools, hotels.
C2, low	Rural areas, depots, sport halls.
C3, medium	Urban, industrial and coastal atmospheres with low salinity, production rooms with high humidity and some air pollution (e.g., food processing plants, laundries, breweries, dairies).
C4, high	Industrial and coastal areas with moderate salinity (e.g., chemical plants, swimming pools, coastal ships, boatyards).
C5, very high	Industrial areas with high humidity and aggressive atmospheres and coastal areas with high salinity, metallic structures with almost permanent concentration and high pollution.
CX, extreme	Offshore areas with high salinity and industrial areas with extreme humidity, aggressive atmosphere, and sub-tropical and tropical atmospheres. Industrial areas with extreme humidity and aggressive atmosphere.

Owing to environmental concerns, eco-friendly coatings solutions for corrosion protection of metals are in high demand in almost all industrial sectors. The need for sustainable technologies capable of performing as well as traditional ones is particularly important for applications in highly aggressive environments such as coastal areas. Currently, there is a huge number of environmentally friendly anticorrosive marine coating technologies under research and in the development stage, among which the most important are:

(i). improved low-VOC (e.g., high-solids, solvent-free) and UV-curable coatings [99], and water-based coatings with better performance;
(ii). anticorrosive coatings incorporating bio-based polymeric resins [100] and natural compounds such as green corrosion inhibitors [101,102];
(iii). addition of non-toxic compounds such as non-isocyanate [103] polyurethane-ureas (NIPUUs), non-toxic ion-exchange [104], graphene [86], or magnesium salts [105] as replacement for conventional toxic anticorrosives such as zinc, chromates, and zinc phosphate ones [106,107];
(iv). biodegradable coatings [108];

Low-VOC and solvent-free anticorrosive coatings are already widely used in marine (e.g., water ballast tanks of ships) and offshore industries. Epoxy coatings with a solid content between 70 and 100% are usually applied as primers and intermediates coats on ships [109], wind power structures [110], and oil and gas pipelines and platforms [65]. High solid PU coatings are also employed, but are preferred as topcoats, for atmospheric exposures due to their superior UV resistance. Topcoats for submerged zones are primarily applied to prevent biofouling, especially on ship hulls in order to minimize drag resistance and fuel consumption [109]. Moreover, biofouling is related to microbially influenced corrosion (MIC) [111], which is a serious issue for pipelines and submerged storage tanks since it can induce detrimental forms of localized corrosion [112]. The attachment of marine organisms also affects the performance of anticorrosion coatings. Several reviews published in the literature provided an overview on environmentally friendly antifouling coatings and its application in marine environments [113–115]. Powder coating is a solvent-free technology, which is experiencing a rapid growth in the protective coating market. Powder coatings are used in many household appliances, aluminum products, and automotive parts. Their associated finish is usually harder and tougher than those obtained using conventional liquid paints. Epoxy powder coatings, known as fusion bonded epoxy, are especially indicated for corrosion protection of submerged pipelines, used as a single layer or in a multilayer coating system, providing very good barrier properties, wear resistance, and adhesion to the metal surface [116]. However, high solid and solvent-free technologies present a higher cost than traditional solvent-borne ones, currently. Along with this, the main challenge in this domain is to increase the resistance of the coating system to the chemical and physical stress encountered during service in order to reduce the operation and maintenance costs and extend the service life of metallic structures, including offshore [41,65].

Water-based paints are currently applied to protect metallic structures at corrosion levels that are relatively low or moderate, corresponding to C2/C3 (ISO 12944) [117,118]. However, innovative water-based thin film [119], acrylic [120], Zn-rich [121], and silane [122] primers; and urethane, epoxy and acrylics topcoats [123] have recently been launched to the market to be applied under more demanding corrosion environments, found for instance in industrial coatings (e.g., containers), transportation coatings [123], building and construction coatings [124], and heavy-duty coatings (e.g., bridges, offshore, marine) [125,126]. They are applied to new construction and steel repair applications in buildings, airports, civil structures, and power generation installations where long protection and environmental performance are a must.

7. Conclusions

Despite the corrosion phenomena having been studied extensively over decades, corrosion control and management using eco-friendly solutions are still a challenge. New health and safety regulations imposed on chemicals and coating manufacturing together with an increased consumer environmental awareness and demand for safer products are pulling the marine and protective coating industry in the direction of circularity and sustainable development. However, relevant issues remain to be addressed. The switch from petroleum-based to bio-based coatings is still hindered by the cost, even if the great potential of bio-based binders is clearly recognized. Furthermore, the comparative analysis of the environmental impacts of bio-based materials and conventional ones (fossil-based) is key to determine the long-term benefit of environmentally friendly coatings.

In the case of water-based coatings solutions, despite being already available in the market, especially in the epoxy segment, more efforts are needed in the optimization of organic coating formulations to achieve the performance of the corresponding solvent borne alternatives. Another factor limiting the transition to sustainable coating is that raw material suppliers have the preference to substitute one component for another instead of developing innovative formulations based on greener chemistries.

The accomplishment of all these expectations is a great challenge for both academia and industry and will certainly stimulate the marine and protective coating sector in the coming years. To the best of our knowledge, environmentally friendly superhydrophobic coatings based on natural waxes, fatty acids, proteins, cellulose derivates, and biomass is one of the technologies with the highest potential to reach the market.

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