Nowadays, steel and light alloys, such as aluminum, magnesium, and titanium, represent most of the primary components of metallic structures in many applications. Steel is known for its availability, high strength, and cost-efficiency [1]. Aluminum stands out for its excellent strength-to-weight ratio, easy casting, high thermal conductivity, and reasonable corrosion resistance [2,3]. Magnesium is somewhat similar to aluminum but is lighter and less corrosion-resistant [3]. Finally, titanium alloys are a good option when either biocompatibility, a high tensile strength, or elevated temperatures (working temperatures around 540 °C) are required [4]. However, the corrosion of these alloys remains an important challenge in terms of durability and safety, since, in addition to their susceptibility to environmental conditions, they can form local microgalvanic couples at intermetallic sites [3,5,6]. To address these issues, polymer coatings are one of the simplest and most efficient protection strategies, limiting the exposure of the metal to corrosive environments. Hence, the development of high-performance smart/self-healing coatings that significantly improve the metal’s lifetime is of the utmost importance and its methods of obtention and action must be thoroughly investigated.

The challenge of developing multifunctional anti-corrosion coatings has urged research to meet the demanding requirements of modern technologies. New metal alloys and extreme environments such as temperature and pH variation, presence of salts, microorganisms, and UV radiation, just to name a few, put the use of conventional polymer coatings into question. In this scenario, the increased demand for durable solutions is driving manufacturers to produce new materials that need to be environmentally friendly and provide optimum protection for the metal under harsh conditions. In addition, the trend towards circular economy has also implemented a more demanding model of production and its implications include the development of self-repairable barrier coatings.

Important advances in the protective coatings field were achieved when the nanophases of ceramic materials were incorporated into standard polymer coatings, resulting in the so-called “hybrid coatings” [7]. The synergy seen when combining the hydrophobic barrier of polymers with the high thermal and mechanical features of inorganic phases results in a unique material with improved properties. For instance, improvements in the adhesion of acrylic coatings to metal substrates from 6.7 to 26.3 MPa have been reported when proper amounts of silica nanoparticles were added to the organic phase [8]. Additionally, thermal [9,10] and mechanical [11,12] properties can be significantly improved by adding an inorganic nanophase in optimized amounts and under optimal conditions.

The concept of self-healing coatings meets the circular economy premises and has attracted a lot of attention from industry and academia. Achieving actual self-healing, however, is not an easy task. Conventional paints have been designed and in use since the early 1900s, primarily to promote a physical barrier between the metal and the environment. Additionally, for decorative purposes, pigments were also incorporated [13]. Over time, a subsequent increase in the complexity and functionality of coatings led to the incorporation of corrosion inhibitors such as phosphates, benzoates, chromates, cerium and molybdates salts, amines and amides, and sulfur compounds, among several others, into polymer
coatings [14–16]. Nonetheless, the concept of self-healing or self-repair in biological systems was pioneered by White et al. in 2001 after incorporating microcapsules containing a monomer and catalyst that regenerated cracks in epoxy resins [17].

Recent studies have demonstrated that the addition of micro- or nanocapsules containing organic or inorganic healing agents, reversible covalent bonds (of polymers), shape memory polymers, vascular networks, and organic or inorganic corrosion inhibitors are efficient approaches to promote coating repair after damage. It has been found that the reparative action can be either triggered autonomously or through external intervention (pH, temperature, UV light, mechanical action, chemical reactions, etc.) [18–20]. Regardless of the action type, the passive layer’s integrity should not be compromised when additives are incorporated into coatings. Therefore, the smart system’s size, complexity, and costs should be considered when designing new self-healing coatings [6,20–23].

In recent decades, the advances in polymeric coating systems resulted in technologies capable of solving issues such as a faster curing time, improved adhesion to the metal substrate, higher performance, and environmental safety [24,25]. Despite all these advances, self-triggered smart coatings that can reversibly regenerate coatings after failure, extending their safety, lifetime, and functionality, need to be implemented in the market.

The use of inorganic inhibitors, such as inorganic salts [26–36], organic molecules [37,38], or carbon dots [39,40], has shown an excellent cost–benefit ratio and low complexity, making this approach very promising for applications in a wide range of industries. When loaded in a concentration range of 500 to 2000 ppm, these additives do not significantly affect the structural integrity and adhesion of the coatings [26,27].

The nano- and microcapsule systems containing inorganic or organic healing agents [17,20,41–46] have shown good activity against corrosion and mechanical damage, liberating active agents by crack-induced rupture. Similarly, ion exchange systems, such as lamellar double hydroxides (natural or synthetic clays), can release considerable amounts of inhibitor compounds or ions that interact with corrosion products, thus forming a passive layer [47,48]. Sulfur-containing compounds exhibit the ability to form reversible covalent disulfide bonds in the damaged zones [49,50], thanks to the dynamic nature of the S-S cross bonds of tetrasulfide groups [51].

Finally, the integration of microvascular networks, capillaries, or sensors inspired by biological circulatory systems has been explored as an alternative in the release of self-healing agents for the detection and repair of multiple damages in coatings. The incorporated three-dimensional nanostructures act as reservoirs for the storage of healing substances such as 8-hydroxyquinoline, Ce(III), Li₂CO₃, among others [6,52–54], which are released in the vessels through capillary action to the damaged region. For these systems, a maximum efficiency of regeneration over some cycles can be observed, resulting in an increase in the coatings’ lifetime, although the costs and complexity for its scalability need to be considered [6,20–23].

Considering all these approaches, some of the most challenging factors in producing smart anticorrosive coatings include: (i) the selection of effective, stable, and environmentally friendly systems that provide fast restoration after failure; (ii) the incorporation of agents that largely preserve the integrity of the physical barrier property; (iii) functional compatibility between additives and the coating; (iv) the employment of cost-effective, green, and simple methodologies; and (v) development of reversible healable coatings with reproducible performance over several cycles. Even though significant advances have been made toward more sustainable high-performance and self-healing films, the latter criterion remains the most challenging. New studies are necessary to further develop smart coating systems that provide efficient, reproducible, scalable, economical, and green solutions for the industrial sector.
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