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## Chapter 9

# Polymeric nanoparticles and their composites in corrosion inhibition

**Abstract:** Metal hardware is inherently prone to corrosion. Substantial research has been undertaken to explore to supersede this challenge. Initially, paints, pigments and organic coatings were utilized to circumvent metal corrosion. Lately, polymer composites and nanocomposites have become favored anticorrosion agents, especially epoxy, polyethylene glycol, polyaniline and polystyrene. The future research on polymer nanocomposites has the potential to address the current challenges of metal corrosion.

**Keywords:** Corrosion, corrosion inhibitors, nanoparticles, nanopolymers

## 9.1 Introduction

Today, nanotechnology is a swift progress in Garea. Nanoparticles are between 1 and 100 nm in size due to their exclusive physical and chemical properties. The most important field of application of nanoparticles in industry is that they have a high specificity to protect metals against corrosion in adverse conditions [1, 2]. Metals are indispensable for the industrial life because they are electrical and thermal conductors and have desirable freezing and boiling points, tensile strengths, high mass/volume ratios and plastic behavior. The omnipresence of free oxygen is the noxious enemy for these precious elements, giving rise to corrosion [3, 4]. Various techniques are used to reduce the corrosion rate such as the coating of metal surfaces and the use of corrosion inhibitors [5]. The inhibitors are applied on the metal surface as thin films to insulate it from its environment. They can be organic and inorganic in chemistry. A common drawback in the use of these expensive substances is that they are

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detrimental to human health. In this regard, nanoparticles and nanocomposites stand as better corrosion inhibitors as they are relatively more harmless, biodegradable and less expensive [6–8].

## 9.1.1 Properties of corrosion

### 9.1.1.1 Corrosion definition

All materials, or more generally all kinds of products and structures made using materials, are generally exposed to physical wear during their use. The underlying cause of this wear can be mechanical, thermal, chemical, electrochemical or microbiological. In terms of metals, the main reason for this wear problem is corrosion. According to DIN EN ISO 8044, corrosion is defined as the significant loss of function of metals, the environment or the technical systems of which they are a part, as a result of the physicochemical interaction of metals with their environment [9]. This interaction is usually electrochemical [10].

The main reason why metals can easily corrode even in normal operating environments is that metals irresistibly tend to return to their stable state. Almost all of the metals exist in nature as low-energy oxide compounds, that is, in a stable state. The foundation of the corrosion problem was laid with the first examples of human beings being able to obtain them by processing metal mines in nature, thanks to metal mining, which dates back to prehistoric times. Large amounts of heat energy are transferred to the metal oxides extracted from the mines to separate them from the oxygen in the blast furnaces, forcing the metals to be in a thermodynamically unstable state. This transferred excess energy is the driving force in the initiation of various corrosion reactions later on. When the corrosion reaction is complete, excess energy is released and the metal (for example, iron and steel) returns to its stable, i.e. oxidized state, completing the cycle shown in Figure 9.1 [10, 11].

It is thought that the economic loss caused by the corrosion of metals is at the level of trillions of dollars worldwide and it is more than 3% of the world's gross national product, namely GDP [12]. In addition to this huge economic cost, corrosion poses a serious risk for both humans and the environment. The destruction of thousands of houses and the death of hundreds of people in the explosion that took place due to direct corrosion in Guadalajara in 1992 is one of the biggest examples that reveal the magnitude of this risk. As a result of the leakage that occurred in the transit pipeline belonging to BP in Prudhoe Bay in 2006, the spillage of approximately 267,000 gallons of crude oil into the environment for five days also revealed the magnitude of the environmental risk that corrosion may cause. As can be understood from these two examples, it is of great importance to develop new products and techniques that can prevent or slow down corrosion, considering the accidents that corrosion may cause and the huge economic loss [10].

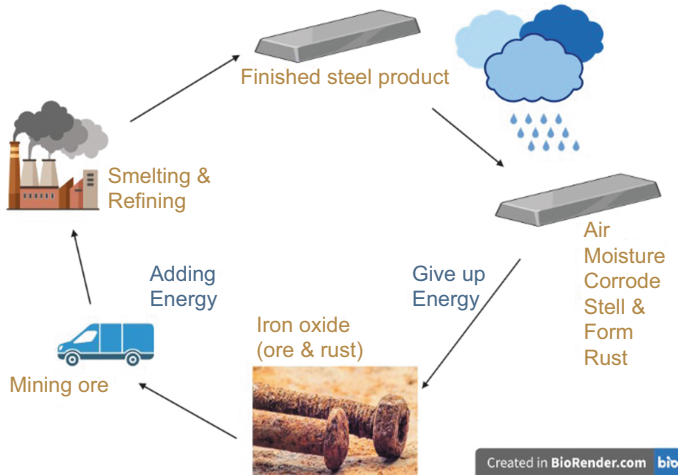


Figure 9.1: Corrosion cycle in metals.

### 9.1.1.2 Types of corrosion

In general, corrosion can be examined in three main groups according to the detection methods [10]:

#### *Corrosion types detectable by visual inspection*

- Uniform corrosion: A type of corrosion in which metal loss occurs at almost the same rate across the entire surface.
- Local corrosion (pitting corrosion, crevice corrosion): A type of corrosion in which metal loss occurs in certain areas.
- Galvanic corrosion: A type of corrosion caused by electrical contact between dissimilar conductors in an electrolyte.

#### *Types of corrosion that can be detected using special inspection instruments*

- Intergranular corrosion (stripping corrosion): The type of corrosion that takes place at the grain boundaries in the metal structure.
- Selective corrosion: A type of corrosion that results from the selective dissolution of one or more of the components in an alloy.
- Velocity-acting corrosion (erosion–corrosion, cavitation and erosion): Erosion–corrosion caused by high velocity flow, cavitation occurring at higher velocity flow, injury caused by vibrational movement of the surface with the surface in close contact under load.

#### *Corrosion types that can be detected with the help of a microscope*

- Cracking event (stress corrosion, cracking, fatigue): Corrosion types that cause mechanical events.

- High temperature corrosion (internal attacks, calcification): Types of corrosion caused by high temperature.
- Microbial corrosion: Types of corrosion caused by certain types of bacteria or microbes.

### 9.1.1.3 Corrosion measurement techniques

The methods used in the measurement of corrosion behavior can be broadly divided into two main groups: electrochemical and nonelectrochemical techniques. Nonelectrochemical techniques are mass loss, pitting and crack formation rate, surface measurements, analytical methods and mechanical testing. Mass loss tests are the simplest and most widely used corrosion and inhibitor test method and are used to monitor total metal thinning and local corrosion types as a function of inhibitor concentration. The corrosion test-strip method follows the principle of monitoring the corrosion development by visual, microscopic or mass loss methods by exposing test strips of a specified standard weight, size and shape to a corrosive environment with and without inhibitor for 14-day period. With this method, although the safe lifetime can be predicted depending on the rate of corrosion, it can provide little information about the specific events that cause the total corrosion damage in the specified period [10].

Since corrosion is basically a process involving electrochemical oxidation and reduction reactions, it is much more practical to use electrochemical measurement methods for corrosion tests, but they can also provide more detailed information [13]. Electrochemical measurement techniques used in corrosion tests are potentiodynamic polarization measurements, electrochemical impedance measurements, electrochemical noise measurement, scanning kelvin probe and scanning-vibrating electrode technique [10].

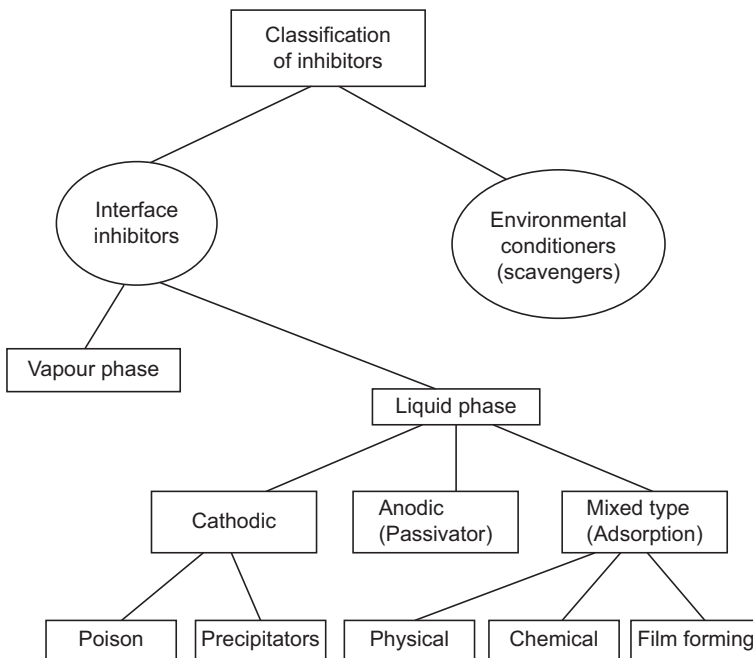
### 9.1.1.4 Corrosion cost and outcome

Corrosion is a worldwide phenomenon and leads to the 3.4% loss in world's income. Thus, direct and indirect loss amounts to US \$2.5 trillion [14]. Direct losses arise from the damaged or faulty machinery infrastructure and the cost of maintenance [15, 16].

One detrimental outcome of corrosion is the inadvertent leakage of contaminated liquids from transporting vessels or storage tanks. In 2011, earthquakes and tsunamis caused the reactors to melt down [17], and in 2013, hundreds of tons of wastewater leaked from a storage tank because of the corrosion around the faulty seals in Japan [4]. On November 22, 2013, the Donghuang II oil pipeline blew up by the ignition of vaporous oil in eastern China [18–20].

### 9.1.1.5 Corrosion protection methods

It has been estimated that application of the best metal corrosion prevention measures may reduce annual corrosion costs up to 35% [21]. Various strategies have been adopted to combat the menace of corrosion: (i) designing a material or system to avoid cracks, excessive speeds or local turbulence [22]; (ii) selection of corrosion resistant materials for specific applications; (iii) electrochemical (anodic and cathodic protection); (iv) coatings; and (v) use of corrosion inhibitors. Although no metal is completely immune to corrosion, metals react differently to corrosion in different environments, so by controlling and understanding the application environment, metals with good corrosion resistance can be selected [23]. Anodic protection is employed to shield protect carbon steels in extreme pH environments [24]. Coatings (painting, coating and lubrication) involve covering a metal surface with a protective film that forms a physical barrier to corrosive surroundings [25]. Corrosion inhibitors are compounds that are added in small quantities to destructive environs to lessen the level of corrosion [22]. Corrosion inhibitors are classified by their inhibition mechanism (Figure 9.2). They are liquid or vapor films at the metal/environment interface [20, 22].



**Figure 9.2:** Classification of inhibitors [20, 22].

## 9.1.2 Nanomaterials as corrosion inhibitors

### 9.1.2.1 Nanoparticles

Shifting the focus of the search from organic coatings to the use of nanomaterials has been prompted by the proposition that the smaller size of the components of nanomaterials will increase adhesion to metal surfaces. Research in this field has mainly driven by factors as follows:

- Negative opinions on the link between hexavalent chromium and carcinogenicity (Figure 9.3) [26]
- Hazardous volatile organic compounds
- The sufficiency of very small amounts of nanomaterials to obtain a thin, sticky film

The issue of the link between hexavalent chromium and carcinogen etc	Due to hydrolysis $\text{Cr}^{6+}$ exists in moderate acidic conditions as an oxo ion
	Hydrolysis of $\text{Cr}^{6+}$ has an impact on corrosion protection/inhibition
	Damage to DNA is not due to $\text{Cr}^{6+}$ or $\text{Cr}^{3+}$ but by the “debris” resulting from the conversion of $\text{Cr}^{6+}$ to $\text{Cr}^{3+}$
	$\text{CrO}_4^{2-}$ “aşone” is not responsible for the damage of DNA
	Inhibition of corrosion by chromates could be attributed to irreversible adsorption of chromates on metals and metal oxide surfaces

**Figure 9.3:** Alleged link between hexavalent chromium and cancer [26].

Ultrathin silane films including small amounts of nanoparticles have been shown to provide exceptional protection to metals [27]. The procedure involved the following steps: colloidal solutions were obtained by loading silica nanoparticles into bisulfur silane. After the metal was then immersed in this solution and dried, a very thin film formed on the metal surface. In another instance, CeO nanoparticles loaded in silica–alumina hybrid coating have been successful in the inhibition of Cu corrosion [28]. In another application, electrochemical performance of the cerium–silane hybrid coating has been shown to rely on the concentration of ceria nanoparticles. This information illuminated the significant effect of nanoparticle concentration on the barrier properties of silane films [29].

An electroless technique has been chosen to deposit Ni–phosphorus (P) and Ni–P–Re on copper disks on metallic surfaces [30]. This Ni-containing film has been found to be helpful in automobile and electronics industries. Corrosion resistance has been further enhanced by adding nano- $\text{S}_2\text{O}_2$  particles into the Ni–phosphorus coating [31]. In another application, brass surface has been coated with monolayers of PropS-

SH (3-mercaptopropyl trimethoxy) silane tempered with  $\text{La}_2\text{O}_3$  nanoparticles [32]. The latter filled the holes in the silane film and increased the density of the film. Conversion of some oxide nanoparticles to hydroxide caused blocking of the cathode sites by the resulting hydroxides [33]. In this way, it was possible to effectively prevent the access of corrosive substances to the metal surface. Clay nanoparticles have been combined with cerium salt to increase the corrosion resistance of the mild steel coating due to the synergistic effect between the nanoparticles and the clay [33]. In addition, both corrosion inhibitions and antibacterial properties of Ag nanoparticles have been explored for aluminum in HCl solution [34]. Ag nanoparticles have effectively inhibited corrosion in both cases [26, 34].

### 9.1.2.2 Nanopolymers

Corrosion of metals is an electrochemical reaction with the surrounding milieu, where the metal behaves as the anode and oxidized (Figure 9.1) and the oxygen existing along with water is the cathode, producing hydroxyl ions [1, 2]. Corrosion of metals and metal alloys is also encouraged thermodynamically. Nonconductive polymers like epoxies have superior compressive strengths, and polymers reinforced with nanoparticles have been used as the corrosion-protecting agents. Nanosilica-filled epoxy, for example, improves durability and toughness and yields high thermal stability [35]. Polymers such as polyaniline (PANI), polythiophene, polypyrrole and polyacetylene show conductive and anticorrosive properties, depending on their oxidation state [36]. Here, the self-healing ability of polymers appears to play an important role in protecting metals. Conductive polymers can also prevent oxide formation. PANI stabilizes the passive state of stainless steel against sulfuric acid [37]. PANI/partially phosphorylated poly(vinyl alcohol) nanoparticles in the epoxy matrix have displayed good corrosion resistances [38–40].

### 9.1.2.3 Nanocomposite as corrosion inhibitor

Nanocomposites hold another means to tackle corrosion. Polymers and nanomaterials are used to produce nanocomposites. In general, organic and inorganic components constitute a nanocomposite [34]. The inorganic components of the nanocomposite provide its tackiness, high ductility and good mechanical rigidity, while the organic components contribute to its flexibility and reduce structural defects. The commonest polymers in the preparation of nanocomposite coatings are epoxy [41, 42], polyurethane [43], polyethylene glycol (PEG) [44], PANI [45], polystyrene [46], polyacrylic [47], polyvinyl alcohol [48], polypyrrole [49] and polyamide [50]. Metal nanoparticles [45, 51] and their oxides [52], carbides [53] and phosphate [54] generally form the inorganic component [8].

Carbon nanoparticles (fullerene, nanodiamond, graphene, graphene oxide, carbon nanotube, carbon black, nanoclay, silica and titania nanoparticles) have been incorporated into matrices to increase the corrosion resistance of polymeric nanocomposites. To improve the performance of nanocomposites, functionalization is adopted to achieve better interfacial bonding and charge transfer properties of the matrix/nano filler [55]. The addition of functional nanoparticles, besides preventing the diffusion of penetrating species, strengthens the nanocomposite structure [56]. This process can also ease friction and increase wear resistance of the base material [40, 57, 58].

### 9.1.3 Conclusions

Metals have desired inherent characteristics like high electrical conductivity, strength, robustness and toughness. This is why metal is preferred in various structural, engineering, electrical and electronic uses. However, metals have a tendency to react with surrounding oxygen and rust. The decomposing environs usually determine the magnitude of corrosion and the underlying mechanisms. Corrosion affects mechanical strength and causes environmental pollution at the same time [47]. Polymers can be exploited as corrosion inhibitors, although their effectiveness is inadequate [48]. In order to produce new anticorrosion polymer nanocomposites in advanced engineering uses, various aspects of these materials must be investigated. The corrosion resistance of nanocomposite coatings essentially depends on the distribution of the nanofiller in the matrix, and a homogeneous dispersion is often a difficult task. Here, in situ polymerization and rapid sonication methods can be convenient.

Temperature and environmental factors directly affect the corrosion resistance of coatings. Nanocomposite coatings endure temperature vagaries and aging better than pure polymers. The incorporation of functionalized nanoparticles can enhance the interaction between matrix/nanophils [49]. It is also important to understand the corrosion inhibition mechanism and adhesion properties of a particular nanocomposite [40, 50, 51]. The adsorption energies of corrosion inhibitors need to be studied by means of thermodynamic and molecular dynamics simulations. Nanocomposites also need to be investigated for nonwetting, surface roughness and anticorrosion properties using contact angle, salt spray testing and scale prevention. Future aerospace industry entails new stratagems to gain insight into the corrosion mechanism.

For future fuel cells, graphene-based nanocomposite coating can increase bipolar plate hydrophobicity and replace chromium and other potentially toxic chemicals. In addition, polymer/CNT and polymer/graphene have excellent corrosion resistance and durability properties for use in next-generation fuel-cell bipolar plates. Advanced nanocomposite can serve as better alternatives to current artificial bones and tissues. Current consciousness has opened new horizons in corrosion research to adopt green nanomaterials.



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