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Review Article

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Polymer-based Corrosion Inhibitors: A Comprehensive Review and Modification Strategies

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Abstract

The use of polymer-based corrosion inhibitors has garnered significant attention as an effective means to combat corrosion and prolong the durability of metallic materials. This review article provides a detailed examination of recent advancements in this field, with a specific focus on the strategies employed to enhance the performance of polymer-based corrosion inhibitors. The principles of corrosion inhibition and the advantages associated with polymer usage, the review explores diverse types of polymers utilized as corrosion inhibitors, encompassing synthetic, biopolymer, and conducting polymers. The discussion encompasses synthesis methods, corrosion inhibition mechanisms, and the relationships between polymer structure and properties. Furthermore, the article emphasizes the significance of comprehending the interplay between polymers and metal surfaces in achieving effective corrosion protection. Various modification techniques are also investigated, including chemical modification, copolymerization, the incorporation of functional groups, the formation of nanocomposites, and surface modification. The challenges and prospects in the field are addressed, underscoring the need for innovative approaches such as stimuli-responsive polymers, smart coatings, and self-healing systems. This comprehensive review serves as a valuable reference for researchers and professionals in the corrosion science and engineering domain, consolidating existing knowledge and providing directions for further research endeavors.

Keywords

Polymer, Corrosion, Corrosion inhibitor, Copolymerization, Nano composites

Introduction

Corrosion arises from a chemical process where metal undergoes a reaction with oxygen and water, resulting in the creation of stable metal oxides. The accumulation of these oxides poses a threat to the metal, leading to its gradual degradation. An observable sign of corrosion is the emergence of a reddish-brown coating on the metal's surface. Corrosion poses a significant challenge in marine settings, notably within the oil industry and navy. Unfortunately, a conclusive remedy for this problem remains elusive at present [1, 2]. The occurrence of corrosion results in a range of losses, encompassing economic consequences that directly affect key industries like thermal plants, nuclear plants, and the petroleum industry. These industries play a vital role in the nation's economy and corrosion poses significant challenges for their operations. Numerous mishaps related to corrosion failure that result in safety risks, financial losses and other factors have been reported. Some of the most well-known incidents include the Carlsbad pipeline explosion accident (New Mexico; 19 August 2000), the Aloha Boeing 737 airlines accident (US; 18 April 1988), the Guadalajara sewer explosion (New Mexico; 22 April 1992), the Gaylord Chemical Explosion (Louisiana;

23 October 1995), the Sinking of the Erika (Brittany, France; 12 December 1999), the Silver Bridge Collapse U.S. (US; 15 December 1967), the Bhopal MIC [3-10]. Consequently, the nation's economy bears the brunt of these challenges. Furthermore, corrosion gives rise to environmental losses as the formation of reddish-brown rust on metals leads to the emission of rust particles into the surrounding environment, causing pollution.

To gain a deeper understanding of the corrosion process, let's explore an example that specifically showcases iron as the representative material. During corrosion, a series of reactions occur at the anode, which can be described as follows [11, 12].

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (1)$$

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^{-} \quad (2)$$

At the cathode, the following reaction takes place:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad (3)$$

$$Fe^{2+} + 2Cl^{-} \rightarrow FeCl_2 \quad (4)$$

$$Fe^{3+} + 3Cl^{-} \rightarrow FeCl_3 \quad (5)$$

In the presence of sodium chloride (NaCl), additional reactions occur because of subsequent processes. These reactions involve the combination of corrosion products with moisture (water), leading to the production of hydrochloric acid (HCl).

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \quad (6)$$

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl \quad (7)$$

Although it is not feasible to completely stop the corrosion process, we can implement strategies to minimize its rate. In this review article, we primarily concentrate on polymer-based inhibitors due to their ability to encompass various corrosion prevention techniques. These inhibitors have proven to be effective in slowing down the corrosion process.

Corrosion Protection

Corrosion protection is a multidisciplinary field that requires expertise in materials science, engineering, chemistry, and environmental science. It aims to ensure the longevity, reliability and safety of metal structures and components, extending their service life and reducing the economic and environmental impact of corrosion. By employing appropriate corrosion protection techniques, industries can optimize performance, reduce maintenance costs, and improve safety and sustainability. We can protect metal from corrosion in many ways like material modification, surface coating, design and corrosion inhibitor.

Metal surface modification

In material modification we basically modified a specific material. Throughout human history, functional coatings have been employed to enhance the surfaces of various materials. Ancient examples involve the preservation of early metallic tools and artifacts, such as iron, brass, and silver, through the application of substances like gelatin, animal fat, beeswax, vegetable oils and various clay minerals. Early humans sought after properties like brightness, water repellence, corrosion protection, wear resistance and lubrication. As time progressed, the concept of functional coatings underwent significant development, resulting in a multitude of modern techniques for surface functionalization. Nonetheless, certain ancient surface modifiers, when skillfully manipulated and engineered, continue to find utility due to their exceptional characteristics [13].

Surface coating

Multi-functional coating research necessitates a highly interdisciplinary approach that includes a range of facilities and skills, including molecular and mesoscale computer-based simulation; adaptation of adsorption and curing mechanisms that may be known from substrate pre-treatment and coating technology or adhesive bonding; encapsulation technology or particle-in-matrix formation technologies; analytical tools for quickly characterizing the performance of the coating [14-16]. Surface coating for protecting metals from corrosion remains a popular and effective method in the present time. In the past, when it came to safeguarding iron, people relied on applying oil paint. However, with advancements in technology, a wide range of coatings are now available, tailored to specific metals and their unique characteristics. The interaction between the inhibitor and metal surface in surface coating exhibits a robust and significant attractive force, which holds great significance in corrosion protection. They follow Langmuir adsorption isotherm in this adsorption isotherm the particle that going to be adsorbed are independent from the neighboring site on the surface. Carbon steel can be effectively protected using TGEDA-MDA, a commonly utilized protective coating [17]. On the other hand, low carbon steel can benefit from coatings like polyvinylpyrrolidone (PVP) and polyethyleneimine. These coatings serve as a protective barrier, shielding the metal surface from corrosive environments and significantly prolonging its lifespan. Apart from carbon steel, various other metals can be effectively shielded against corrosion through the application of specific coatings. For instance, copper can be protected by employing cadmium azide and nicotinate ligand as a coating [18]. Aluminum can be safeguarded by utilizing polypyrrole/aluminum flake coatings. Iron surfaces can benefit from coatings such as N-vinyl-2-pyrrolidone and PVP, while steel can be shielded with coatings like PDMAS/TiO_2 epoxy hybrid nanocomposite, epoxy ester–siloxane–urea hybrid polymer, polyaniline (PANI) [19], and TiO_2 nanotubes [20], for mild steel inhibitor precursor (Inh) [21], Xanthan gum [22], Dextrin-graft-polyvinyl acetate (Dxt-g-PVAc) [23] among others. These specialized coatings act as protective barriers, effectively preventing corrosion and preserving the structural integrity and durability of the metal surfaces.

Design

To investigate corrosion protection is crucial to establish the initial configuration to the systems by considering molecules, atoms or repeating units like crystalline inorganic systems or polymer chains as the fundamental building blocks. Additionally, the interactions between these units require careful parameterization, which can be informed by data from the literature, calculations, or experiments.

A computational approach should also be chosen in accordance with the precise time and length scales pertinent to the characteristics and systems under study. Making the right choice will guarantee that the approach can be imitated accurately. Additionally, modeling methods for polymeric materials, nanoparticles and microcapsules must be used in the creation of coatings or multifunctional materials. The desired properties to be studied include things like the solubility of polymeric materials in various solvent, the behavior of guest species during diffusion within host/guest systems, the analysis of encapsulation and release mechanisms and the understanding of surface effects like adsorption and film formation. As a result, it is essential for understanding the interactions between systems of various complexity and size [14].

Corrosion inhibitor

Corrosion inhibitors are substances that safeguard metals against corrosion and can be categorized into organic, inorganic, natural and polymer inhibitors. Organic inhibitors are effective due to their composition, which often includes polar functional groups like -$CONH_2$, -OCH_3, -OH, -NO_2, -COOH, -NH_2, -$COOC_2H_5$ as well as lone pair and π-electrons with extensive conjugation. These organic inhibitors may cling to the metal surface by physisorption, chemisorption (electron sharing with the metallic), non-bonding interactionsor a mix of both [24-29].

In contrast, inorganic inhibitors are typically employed in high-temperature and high-pressure environments where organic inhibitors may not be suitable [26, 27]. They are composed of inorganic substances that create a protective layer on the metal surface such as chromates, phosphates, molybdates and silicates. In industrial settings like cooling water systems, boilers and pipelines, inorganic inhibitors are widely used [27-30]. Various industries, including oil and gas, automotive, construction and marine sectors, rely on inorganic inhibitors to protect pipelines, storage tanks, metal components of vehicles, bridges, buildings, tunnels, ships, and other marine structures from corrosion [31].

Both organic and inorganic corrosion inhibitors play significant roles in safeguarding metals against corrosion. Their applications can be complementary, as using those in combination can provide enhanced corrosion protection [32-34].

In this paper we will mainly focus on the polymeric inhibitors. In recent years, there has been a notable rise in the use of polymer-based materials across industries as a reliable means to combat corrosion. These materials, which are non-metallic and possess excellent chemical stability, find widespread application through polymer techniques, coatings, and polymer coatings on metal. Their primary purpose is to safeguard non-ferrous metals such as copper and steel from corrosion, effectively tackling the corrosion-related issues encountered by various sectors throughout the country [35].

When choosing an inhibitor for protecting metal against corrosion, several considerations must be considered, such as the desired level of inhibition and the specific mode of action. It is also essential to select a readily available polymer that is environmentally safe [21].

Polymers as an Effective Corrosion Inhibitor

The current focus of research revolves around the utilization of polymers as corrosion inhibitors, offering substantial advantages for both metals and the environment. These polymers play a crucial role in safeguarding metal surfaces against corrosion by establishing a protective barrier. Within this review article, we delve into a comprehensive examination of diverse polymers functioning as corrosion inhibitors. Specifically, we explore the application of corrosion inhibitor precursors (Inh) designed to combat corrosion in magnesium alloys through the employment of macro-arc oxidation (MAO) treatment. This treatment facilitates the integration of corrosion inhibitors into the pores of the MAO membrane [36, 37]. Moreover, the sol-gel method enables the preparation of TiO_2 nanoparticles to enhance the corrosion inhibition [38, 39]. In the case of copper metal, the utilization of cellulose composite demonstrates remarkable corrosion inhibition properties when immersed in a 3.5% NaCl medium [21]. Furthermore, for steel substrates, the incorporation of DBSA-doped PANI in coatings proves to be effective in improving corrosion resistance. Notably, DBSA-doped PANI exhibits favorable dispersibility in chloroform [40, 41]. Additionally, for metals containing 1% and 2% graphene content, polyurea emerges as a corrosion inhibitor of choice [17]. The influence of temperature on corrosion kinetics necessitates the development of a combination of Cadmium Azide and Nicotinate Ligand to assess the associated activation parameters [18]. An epoxy resin (TGEDA-MDA) has been formulated and evaluated as a coating material for carbon steel in a 3% NaCl system, showcasing a significantly high level of protection efficiency, reaching approximately 93% [19]. The synthesis of poly(DAMA-ran-DAMTDB) diallymethyl ammonium chloride utilizing Butler's cyclo-polymerization technique demonstrates its exceptional efficacy in harsh acid environments at elevated temperatures when applied to steel surfaces [42, 43]. To establish a protective barrier between the metal and corrosive media containing chloride ions, molybdate is employed as a corrosion inhibitor, subsequently released to mitigate corrosion. The formation of CNTs/LDH-MoO_4 acts as a formidable barrier against corrosion [44]. Sol-gel nano-coatings generate adherent and chemically inert films under varying temperature conditions, ultimately resulting in the development of micro or nano porous glassy polymer networks [45]. This reduction in processing temperature holds significant advantages as it circumvents undesirable phase transitions typically associated with high-temperature alloy-based coating procedures. The application of the sol-gel technique is extended to encompass the production of thin films or coatings across a diverse range of systems [46]. In 15% HCl medium, a natural polysaccharide known as Xanthan gum, synthesized as XG-g-PAM, demonstrates its effectiveness as a protector of corrosion for mild steel. These inhibitor molecules adhere to the Langmuir adsorption isotherm [22]. To enhance stability and corrosion inhibition efficiency, a larger molecule structure, namely Dxt-g-PVAc is synthesized through the ATRP process [23].

Natural polymer

Cellulose materials can be synthesized using the solvent exchange method [37, 47, 48]. This technique involves repeating cellulose units to create the desired cellulosic material. To further analyze the inhibitor, various techniques such as Fourier transform infrared spectroscopy, scanning electron microscope, dynamic light scattering measurements and electrochemical measurements are employed. One significant advantage of this inhibitor is its ability to form a protective barrier layer on the surface of copper. This facilitates a favorable interaction between the inhibitive species and copper surface at the molecular level. The inhibitive species selectively absorb onto the susceptible metal sites prone to corrosion. Furthermore, the nitrogen atom in niacin possesses a lone pair of electrons that can donate to the copper surface, forming a coordination bond that aids in inhibiting corrosion. The presence of electron-donating groups in niacin-based cellulose composites enhances the electron density on the nitrogen atom, resulting in high efficiency in corrosion inhibition. Additionally, the π electrons present in the aromatic rings of niacin interact with the unoccupied d-orbital of the metal, providing further protection [37].

The adsorption mechanism of Xanthan gum involves the binding of molecules, which is widely acknowledged. It relies on the presence of donor atoms like N, O, S, etc., as well as the characteristics of the vacant d-orbital and metal surface [49, 50]. The metal surface gains a negative charge in HCl solution due to the adsorption of chloride ions and attracting positively charged species already present in the medium. Both in acidic and neutral situations, the inhibitor molecule may successfully cling to the metal surface.

In a neutral medium, the inhibitor molecule displaces water molecules through a chemisorption process and a donor-acceptor mechanism. The adsorption of the inhibitor occurs through four distinct types: (i) Electrostatic interaction between the metal surface and inhibitor molecule, (ii) Interaction between inhibitor and metalvia unshared electron pairs of molecules, (iii) π-electron interaction between inhibitor and metal, and (iv) A combined effect of electrostatic interaction and π-electron interaction [22].

Dxt-g-pVAc follows a similar adsorption mechanism to Xanthan gum, as mentioned earlier. In an acidic environment, inhibitor molecules are adsorbed at the cathodic sites of the metal surface, effectively reducing hydrogen evolution. Conversely, on the anodic sites, the inhibitor molecules are adsorbed through interactions involving the lone pair and electrons of hetero atoms reduce the solubility of metal.

Electrochemical studies have substantiated that the corrosion inhibitor Dxt-g-pVAc exhibits superior corrosion efficiency compared to Dxt. Its adsorption behavior aligns with the Langmuir adsorption isotherm, indicating a favorable adsorption process. The advantage of employing this inhibitor stems from its larger molecular structure, which contains more reactive centers. This structural attribute results in stronger adsorption on mild steel, leading to heightened stability and improved efficiency of the inhibitor's corrosion inhibition properties [23].

Guar Gum (GG) and Cationic Guar Gum (CGG) demonstrate a mechanism of adsorption on metal surfaces like that of Xanthan gum. The presence of their lone pair electrons and the electrostatic interactions between the positively charged inhibitor molecules and the negatively charged metal surface are predicted to cause both GG and CGG to be adsorbed onto the metal surface [51]. It is anticipated that the bulk of the molecules will be in their protonated state given the medium's extreme acidity. It helps the polymer cling to the negatively charged surface of mild steel in the case of CGG because it contains the positive tertiary amine group CHPTAC. Due to the positive charge contained in CGG, the inhibitory activity is shown to be more severe in comparison to GG.

GG and CGG exhibit adsorption mechanisms, involving electrostatic interactions and the presence of lone pair electrons. However, CGG demonstrates a heightened inhibitory effect, likely due to the positive charge it carries, facilitating its adsorption onto the surface of mild steel [51].

Synthetic polymer

The significance of adsorption on metal surfaces is widely known. When an inhibitor is present, it eliminates water from the electrode surface. The copper, cadmium azide and the nicotinate ligand are introduced in an HCl medium, the nitrogen atom in these compounds acquires a positive charge, as mentioned in a before. HCl contains chloride ions, which are highly electronegative and tend to adhere to the copper surface due to electrostatic attraction. This adsorption mechanism creates a composite film where chloride ions are positioned between the copper surface and the inhibitor. The efficacy of this film stems from its ability to cover a substantial area of the metal surface, serving as a protective barrier against corrosion. In the study discussed in this paper, the corrosion inhibitor was evaluated in an HCl medium, and the results aligned with the Langmuir adsorption isotherm, indicating a favorable adsorption process [18].

In various platforms such as Tafel plot, PANI has been tested under different parameters in 3.5% NaCl medium. During these tests, the transition from π to π* was observed, which was measured using ultraviolet spectroscopy. This transition exhibits a bipolar nature. When it comes to PANI coating, it creates a system of ordered polymer bundles that gives corrosive ions room to approach the metal surface. The main mechanism behind the efficiency of PANI coating is this configuration. The initial layer of the conducting polymer is formed on the electrode during the creation of electrochemically generated composite films by raising the insulating coating only a little bit. The conducting polymer then develops, leading to polymerization that spreads throughout the entire matrix. However, in acidic environments, the corrosion resistance provided by polyaniline coatings is very poor, and they tend to degrade within a short period, typically around 15 or 20 min. To overcome this limitation, coating with sulfate-reducing bacteria has been successfully applied to stainless steel electrodes. This approach yields positive results in both acidic and neutral mediums [41].

The construction and automotive sectors use laminates made of the epoxy-ester-siloxane-urea polymer. On the other hand, polysiloxane compounds, known for their hydrophobic nature [17], exhibit excellent corrosion inhibition properties. Among these compounds, polymethyl hydro siloxane is particularly favored due to its non-toxicity, stability in the presence of air and moisture, and its ability to convert carbonyl compounds into alcohols. This compound serves as a cost-effective and environmentally friendly corrosion inhibitor [17]. In the conducted study, the polymer was subjected to testing on graphene sheets, resulting in a strong interfacial adhesion between the graphene and the polymer. This strong adhesion helped to boost the material's hardness, tensile strength, and resistance to wear, fatigue, cracking, and corrosion.

The formation of DAMA-ran-DAMTDB includes convert rapid presence of diallymethylamine using the technique of Butler's cyclopolymerization. This polymer follows the mechanism of chemisorption and corrosion is mitigated from the adsorption of the polymer. In the mechanism removal of proton may occur and as the resultant removal of certain hetero atoms [42]. These heteroatoms generally donate their electron in the 3-d orbital of Iron, this is responsible for the formation of a chemical bond between iron and inhibitor molecules [43]. This occurrence is easily explained by the Langmuir adsorption isotherm (Table 1).

Advantages and Limitations

Polymers have the qualities that make them environmentally friendly, less toxic, and cheap. They have minimum damage to the environment and are easily stored for a long time. In other words, polymers have the quality of preventing metal from corrosion. In general, apply a thick layer of inhibitor. The thickness of the inhibitor is between 250 to 400 micrometers. We know that corrosion depends on temperature. So, it is necessary to develop a polymer which does not change their physical and chemical properties at high temperature and prevent metal from corrosion.

Some polymeric materials have high mechanical strength and their used as the formation of plant-extract polymer like Xanthan gum and cellulose composites as corrosion inhibitors. The features of the environment in which a polymer functions, characteristics of metal surface and electrochemical potential at the interface are just a few of the variables that affect a polymer's ability to act as a corrosion inhibitor. Significant functions are also played by the inhibitor's structure and method of interaction with the metal surface. These factors include the molecule's charge density, molecular size, adsorption process, creation of metallic complexes, and inhibitor occupies metal surface. They also include the active sites of the molecule.

Conclusion

The mechanism of corrosion inhibition involves the process of adsorption, which is influenced by various factors including the type of metal, physicochemical properties of the inhibitor molecule (such as functional groups, electron-withdrawing groups, donor atoms and the electron donation char-

Table 1: Polymeric materials used as corrosion inhibitors.

Metal/Alloy	Inhibitor	Medium	Efficiency	Ref.
Carbon steel	Epoxy resin (TGEDA-MDA)	3.0% NaCl	93.0%	[17]
Copper	Cellulose-niacin composite	3.5% NaCl	94.7%	[21]
Steel	PDMAS/TiO_2 epoxy hybrid nanocomposite	-	99.7%	[20]
Copper	Cadmium azide and nicotinate ligand	1 M HCl	93.3%	[18]
Aluminum	Gum Arabic	0.1 M with and without of KI	75.8%	[52]
Stainless steel	PVP polymers	0.5 M HCl	96.9%	[53]
Steel	Epoxy ester-siloxane-urea hybrid polymer	1 - 2% Graphene	-	[17]
Steel	PANI	3.5% NaCl and 0.5 M HCl	-	[19]
Stainless steel	Cloisite 15A, multiwalled carbon nanotubes and cerium chloride	4 M HNO_3	-	[39]
Mild steel	PANI	-	85.9%	[54]
Iron	N-vinyl-2-pyrrolidone and PVP	1 M H_2SO_4	-	[55]
Aluminum anode	Polyvinyl benzyl trimethylammonium chloride and poly diallyl dimethyl ammonium chloride	Alkaline electrolyte	-	[56]
Low carbon steel	PVP and polyethyleneimine	Aqueous H_3PO_4 solution	89.0% and 90.0%	[56]
Mild steel	Inhibitor precursor (Inh)	3.5% NaCl	-	[37]
Mild steel	XG-g-PAM	15% HCl	86.8% and 92.9%	[22]
Mild steel	DXT-g-PVAC	15% HCl	98.4%	[23]
Mild steel	GG	15% HCl	94.8%	[51]
Mild steel	Gum Acacia-graft-polyacrylamide	15% HCl	94.08%	[56]
Mild steel	Cadmium(II) Schiff base complexes	15% HCl	93.8%	[56]
Low carbon steel	DAMA-ran-DAMTDB	15% HCl	86.5%	[43]
Iron	CNTs/LDH-MoO_4	3.5% NaCl	-	[44]

acteristics of d-orbital) and the electronic structure of molecules. Extensive studies on polymer inhibitors have provided valuable insights into the correlation between their adsorption behavior on metal surfaces and the resulting protection against corrosion. Looking forward, the prospects of polymers as corrosion inhibitors are highly promising. This is particularly significant considering the current concerns surrounding environmentally toxic inhibitors that are not environmentally friendly, contradicting our goals for sustainable solutions. Polymers, on the other hand, offer the advantage of being both environmentally friendly and effective corrosion inhibitors. Therefore, the utilization of polymers as corrosion inhibitors holds tremendous potential in meeting the demand for eco-friendly alternatives in this field.

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None.

Conflict of Interest

None.

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