STM JOURNALS

International Journal of
Advance in Molecular Engineering

Volume 3, Issue 2, 2025
July–December
DOI (Journal): 10.37591/IJAME

https://journals.stmjournals.com/ijame

Review IJAME

Polymeric Coating Applied for Corrosion Protection of Mild Steel in Corrosive Medium

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Abstract

Mild steel is coated with a polymer layer of polybutadiene for protection. However, this coating does not effectively safeguard the metal in environments containing moisture, sulphur dioxide, or chloride. These pollutants interact with the polybutadiene-coated surface, creating a highly corrosive atmosphere. Moisture condenses on the coated metal surface and absorbs sulphur dioxide, forming sulphuric acid. This acid initiates both chemical and electrochemical reactions with the polymer-coated metal, accelerating the corrosion process Chloride ions penetrate the coating through osmosis or diffusion, forming corrosion cells on the metal surface. Oxygen depletion inside and outside the coating further promotes corrosion cell formation. As a result, these pollutants cause both internal and external corrosion by breaking the internal bonds within the polybutadiene layer and weakening adhesion between the coating and the metal substrate. Consequently, the metal exhibits several types of corrosion, including galvanic, pitting, stress, crevice, blistering, and embrittlement To mitigate corrosion in such aggressive environments, nanocoating and filler techniques are employed. Octahydrodibenzo annulene-5,12-dihydrazone is used as the nanocoating material, while magnesium sulfide (MgS) serves as the filler. The corrosion rate of the polymer-coated mild steel is determined using gravimetric methods, while corrosion potential, current, and current density are measured with a potentiostat. Nanocoating is applied using a nozzle spray technique The adsorption behavior of the coating is analyzed using the Langmuir isotherm and Arrhenius equation. Surface deposition and bond formation of the nanocoating and filler materials are evaluated through parameters such as activation energy, heat of adsorption, free energy, enthalpy, and entropy. Experimental findings on surface coverage and coating efficiency reveal that the nanocoating and filler materials form a composite thin-film barrier on the polybutadiene-coated mild steel surface, significantly enhancing its corrosion resistance.

Keywords: Polybutadiene-coated mild steel, nanocoating, filler, pollutants, composite thin film barrier

INTRODUCTION

Protecting materials from corrosion is a highly challenging task. Although complete control over corrosion is not possible, its effects can be minimized through various corrosion mitigation techniques. In material manufacturing industries, it is essential to closely monitor the internal morphology, shape, and design of materials. Materials can be synthesized according to the surrounding environmental conditions [1] without altering their physical, chemical, or biological properties [2], while maintaining thermal stability, durability, and resistance to corrosive environments [3].

Corrosion protection methods [4] such as coatings, inhibitors, sacrificial anodes, and impressed current systems are commonly applied under ambient conditions [4]. Various types of coatings—metallic, nonmetallic, polymeric, and

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Received Date: October 16, 2025
Accepted Date: November 01, 2025
Published Date: November 05, 2025

Citation: Rajesh Kumar Singh, Rizwana Khatoon. Polymeric Coating Applied for Corrosion Protection of Mild Steel in Corrosive Medium. International Journal of Advance in Molecular Engineering. 2025; 3(2): 49–53p.

paint—are available, but they generally provide only short-term protection. Corrosion inhibitors [5] are widely used, especially in the petroleum industry, to control metal corrosion. These inhibitors may be organic, inorganic, or mixed types [4], acting through anodic or cathodic mechanisms. Depending on the corrosive environment, inhibitors can be applied in solid, liquid, or gaseous form [6].

Electron-rich organic compounds such as alkanes, alkenes, alkynes, cyclic, aromatic, and heterocyclic molecules containing nitrogen, oxygen, or sulfur are effective organic inhibitors in petroleum [7], sugar [8], phosphate [9], and pulp and paper industries [10], particularly for controlling the corrosion of mild steel and stainless steel. However, these inhibitors generally offer only short-term protection.

Metallic pipe corrosion can be reduced through anodic protection and impressed current systems, though their performance decreases in highly aggressive environments. Natural inhibitors such as Aloe Vera have been used to prevent corrosion in metallic cans containing beverages, juices, milk, and vegetables. Aloe Vera also serves as a protective agent in acidic soils, helping to preserve the lives of earthworms. Similarly, in polluted urban environments, human skin can suffer from corrosion-like damage, which can be mitigated using Aloe Vera and turmeric-based coatings. Furthermore, nanocoatings and filler compounds are applied to protect polymer-coated metals in effluent-rich environments [11].

Experimental

A mild steel specimen measuring 5 × 10 × 0.1 cm^2 was coated with polybutadiene and exposed to an environment containing moist SO_2 and chloride ions. The corrosion rate of the sample was determined using the gravimetric method at temperatures of 283, 293, 303, 312, and 323 K, with exposure durations of 3, 5, 8, 11, and 14 days [12].

Subsequently, the samples were nanocoated with octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone, and their corrosion rates were again measured under the same temperature and time conditions. These nanocoated samples were further coated with MgS, and the corrosion rates were evaluated once more.

Electrochemical measurements, including corrosion potential, corrosion current, and corrosion current density, were determined using a potentiostat for both coated and uncoated samples. In the potentiostat setup, a platinum electrode served as the reference electrode, a calomel electrode as the auxiliary electrode, and the polybutadiene-coated mild steel sample (with or without nanocoating and MgS layer) functioned as the working electrode [13].

The compound octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone used for nanocoating was synthesized through the following steps:

Scheme 1: Synthesis of 4-Chloro-1,2-Dihydronaphthalene

A solution of 3,4-dihydronaphthalen-1(2H)-one (25 g) in benzene (50 g) was treated with phosphorus pentachloride (30 g) at low temperature. The reaction mixture was stirred for one hour, quenched with sodium bicarbonate solution, and extracted with diethyl ether. After solvent removal using a rotary evaporator, the crude product was purified by silica gel column chromatography to yield 4-chloro-1,2-dihydronaphthalene in 89% yield [14].

Scheme 2: Synthesis of 1,2-Didehydro-3,4-Dihydronaphthalene

4-Chloro-1,2-dihydronaphthalene (10 g) was placed in a two-necked round-bottom flask, and a solution of potassium tert-butoxide (25 g) in tetrahydrofuran (THF) was added at 0 °C. The reaction mixture was stirred for four hours, after which cyclohexene was added as a trapping agent, and stirring continued for an additional two hours. The reaction workup produced 1,2-didehydro-3,4-dihydronaphthalene in 90% yield [15].

Scheme 3: Synthesis of Benzo-Decahydrobiphenylene

The reaction of 1,2-didehydro-3,4-dihydronaphthalene with cyclohexene afforded benzo-decahydrobiphenylene through a trapping reaction.

Scheme 4: Synthesis of Octahydrodibenzo[a,d][8]Annulene-5,12-Dione

The adduct (20 g) was oxidized using sodium periodate (10 g) and ruthenium dioxide (15 g) in a solvent mixture of acetonitrile and carbon tetrachloride. After quenching with water and standard workup, octahydrodibenzo[a,d][8]annulene-5,12-dione was obtained in 87% yield.

Scheme 5: Synthesis of Octahydrodibenzo[a,d][8]Annulene-5,12-Dihydrazone

Octahydrodibenzo[a,d][8]annulene-5,12-dione (35 g) was refluxed with hydrazine hydrate (75 g) for 24 hours. The reaction mixture was cooled in an ice bath, and the resulting solid was collected by suction filtration. The crystals were washed with 150 mL of cold ethanol and dried under vacuum for one hour, yielding octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone in 9% yield [16-18].

RESULTS AND DISCUSSION

Octahydrobenzo[a,d][8]annulene-5,12-dihydrazone was applied as a nanocoating on polybutadiene-coated mild steel, and its surface pores were sealed using MgS filler. Corrosion behavior was examined in marine water under three different surface conditions:

1. Polybutadiene-coated mild steel,
2. Nanocoated with octahydrobenzo[a,d][8]annulene-5,12-dihydrazone, and
3. Coated with both the nanocompound and MgS filler. The corrosion rate was determined by the weight loss method using the equation

$K \text{ (mmpy)} = 13.56\, W / (D\, A\, t)$,

where W represents weight loss (kg), A is the surface area (m^2), D is the material density ($kg \cdot m^{-3}$), and t is the exposure time. Measurements were taken at temperatures of 283, 293, 303, 312, and 323 K, and exposure durations of 3, 5, 8, 11, and 14 days.

The data revealed that the corrosion rate of polybutadiene-coated steel increased in marine water; however, it decreased significantly after nanocoating and further with the addition of MgS filler. The plot of K (mmpy) versus t (days) confirmed these trends. Although the polybutadiene coating alone was susceptible to crevice corrosion due to oxygen depletion, the combined nanocoating and MgS filler formed a composite thin film that acted as a more stable and thermally resistant barrier against corrosive ions. MgS filled the pores of the nanocoating and chemically interacted with nitrogen sites of octahydrobenzo[a,d][8]annulene-5,12-dihydrazone, producing a tightly adhered passive layer on the metal surface.

Temperature effects were studied at 283–323 K for all samples. Corrosion increased with temperature, but both nanocoating and filler markedly reduced this rate, as shown in and (log K vs. 1/T).

Values of $\log(\theta/1-\theta)$ for both nanocoating and filler showed that $\log(\theta/1-\theta)$ decreased with rising temperature for the nanocoating, but increased when MgS filler was added. This relationship, illustrated in ($\log(\theta/1-\theta)$ vs. 1/T), indicated that the combined coating developed a non-osmotic barrier that minimized Cl^- and H_2CO_3 ion penetration.

Surface coverage (θ) was calculated using

$\theta = (1 - K/K_o)$,

where K and Ko represent corrosion rates before and after coating, respectively. Results showed that nanocoating enhanced surface coverage, while MgS filler improved its corrosion mitigation characteristics. (θ vs. T) confirmed this behavior.

Coating efficiency (%CE) was determined by

$\%CE = (1 - K/K_o) \times 100$.

Indicated that both nanocoating and filler increased efficiency, with MgS providing a greater improvement. Activation energy (Ea) values for polybutadiene, nanocoating, and filler were calculated using the Arrhenius equation:

$d/dt (\log K) = Ea / (R T^2)$,

where R is the gas constant. Positive Ea values confirmed that chemical bonding contributed to film formation. Reduced Ea at higher temperatures indicated greater coating stability.

The heat of adsorption (q) for both compounds was determined using the Langmuir equation:$\log(\theta/1-\theta) = \log(A\cdot C) - (q / 2.303RT)$,with results showing linearity, confirming chemical adsorption between the coatings and substrate.

The free energy change (ΔG) was obtained from

$\Delta G = -2.303RT \log(33.3K)$,

where K is the corrosion rate. Negative ΔG values indicated that the coating process was spontaneous and exothermic.

Enthalpy (ΔH) and entropy (ΔS) changes were calculated using the transition state equation:

$K = (RT / Nh) \log(\Delta S/R) \times \log(-\Delta H/RT)$,

where N is Avogadro's number and h is Planck's constant. The results revealed negative ΔH and ΔS values, confirming an exothermic reaction and suggesting that MgS filler arranged itself within the nanocoating matrix in an ordered manner.

Overall, analysis of thermal parameters (activation energy, heat of adsorption, free energy, enthalpy, and entropy) indicated that increasing temperature enhanced surface coverage, while the nanocoating–filler combination formed a chemically bonded, diffusion-resistant barrier against marine corrosion.

Potentiodynamic polarization measurements were conducted using the relationship:

$\Delta E/\Delta I = (\beta a \beta c) / [2.303\ Icorr\ (\beta a + \beta c)]$,

where ΔE/ΔI represents linear polarization resistance (Rp), and βa, βc, and Icorr denote anodic/cathodic Tafel slopes and corrosion current density, respectively. The Tafel plots and corresponding data showed that polybutadiene-coated steel had higher electrode potential and anodic current density, which decreased upon nanocoating and filler application. Both compounds enhanced cathodic current density and reduced overall corrosion potential.

The corrosion rate was calculated by

$C.R\ (mmpy) = 0.1288 \times Icorr \times Eq.Wt / \rho$,

where Eq.Wt is equivalent weight and ρ is material density. Results showed that while the polybutadiene coating alone exhibited a higher corrosion rate, it was significantly reduced by nanocoating and further by MgS filler. The MgS-filled nanocoating formed a composite film with excellent stability in marine environments. Corrosion rates obtained from weight loss experiments closely matched those derived from potentiostatic studies, confirming the effectiveness of the composite protective layer.

CONCLUSION

Octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS fillers were used to enhance the corrosion resistance of polybutadiene-coated mild steel. These materials formed a composite coating barrier on the surface of the base polybutadiene layer. Thermal analysis of the nanocoating and filler materials indicated that the formation of this composite surface barrier was an exothermic process. In a corrosive environment, no corrosion cells were observed. The coating efficiency and surface coverage of the nanocoating and filler materials improved under varying temperatures, atmospheric conditions, and weather changes.

Acknowledgement

Authors thankful for UGC-New Delhi provided financial support for this work. I give my thanks to laboratory staffs for their supports during experimental work.

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