Crosslinked polymer doped binary coatings for corrosion protection

Harleen Kaur[a], Jyoti Sharma[a], Divyansh Jindal[b], Raj Kumar Arya[b,*], Sanjeev Kumar Ahuja[b],
Shashi Bhushan Arya[c]

[a] School of Chemistry and Biochemistry, Thapar Institute of Engineering & Technology, Patiala, Bhadson Road, Patiala, 147004, Punjab, India
[b] Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala, Bhadson Road, Patiala, 147004, Punjab, India
[c] Department of Metallurgical and Materials Engineering, National Institute of Technology, Surathkal, Mangalore, 575025, Karnataka, India

ARTICLE INFO

ABSTRACT

Solvent-based polymeric multilayer coatings prepared by ex-situ addition of crosslinked poly(styrene-co-divinyl benzene) in poly(styrene)-ethylbenzene solution were examined for corrosion protection of mild steel in a simulated water environment equivalent to sea water and acid rain. Electrochemical impedance spectroscopy (EIS) technique was used to determine the corrosion resistance behavior of the prepared polymeric coatings in 3.5 wt % of NaCl aqueous solution. EIS analysis suggested that the sample solution prepared by adding 1% crosslinked polymer in poly(styrene)-ethylbenzene solution, has better corrosion resistance as compared to the sample solutions prepared by adding 3% and 2% of crosslinked polymer in poly(styrene)-ethylbenzene solutions. Scanning electron microscopy (SEM) revealed that substrate coated with polymeric solution prepared by adding 1% of crosslinked polymer in poly(styrene)-ethyl benzene solution showed less corrosion as compared to the substrates coated with sample solutions prepared by adding 3% and 2% of crosslinked polymer in poly(styrene)-ethylbenzene solutions.

1. Introduction

Metals occur in nature in their chemically-stable ore form. When metals are extracted from their ore, they become unstable and so tend to return to their original form. The process of conversion of refined metals to stable oxide, sulphide or hydroxide forms is known as corrosion. In other words, the destruction of metals by chemical or electrochemical reaction with its environment is called corrosion. A few examples related to corrosion in daily life are rusting of iron, copper pots containing greenish colour spots, and white powder on zinc roofing, etc. The prevention of corrosion is very important because it can be harmful to economy and is the reason for several safety issues. Corrosion induces different kinds of losses to economy caused by the deterioration of metals. It can be very dangerous from the safety point of view. It decreases the metallic strength of components of vehicles, airplanes and ships, etc. In chemical industries, corrosion of chemical containers, boilers, and pressure vessels can be very detrimental. The kinds of losses caused by corrosion to economy are direct and indirect losses [1].

Metallic components are needed to be repainted in order to prevent direct losses due to rusting. In case of corroded boilers, mufflers, and pipelines, replacement of these components is necessary. Extra money

is required to galvanize zinc on the surface of steel for corrosion protection. It is very hard to determine indirect losses caused by corrosion. Therefore, from a thorough analysis, some indirect losses are determined. For example, in soap industries, small particles of copper from corroded copper pipes lead to contamination of large bunch of soaps. Small amount of metal particles from corroded container or pipes results in variation of the colour of a dye. During reinstatement of corroded pipes in oil refinery, the production of oil has to stop which results in production loss.

A microscopic level observation of metallic surface shows that the surface of the metal is not uniform. There may be presence of some kind of impurities on the surface. The chemical composition and structure may differ throughout the surface of metal. Anode and cathode can exist simultaneously on the surface of metal. The metallic part act as the anode and the impurities present on the surface act as the cathode. Based on the cathodic and anodic sites of metal surface, corrosion occurs in two different ways, that is, localized and uniform corrosion. In localized corrosion one part of the metal surface act as the anode and other part acts as the cathode. However, in uniform corrosion, the cathodic and anodic parts of the metallic surface cannot be distinguished.

Metallic surface comes in contact with oxidizing agents like oxygen

and water droplets. The part of the metal surface inside the water droplet act as anode and the other part act as cathode. The anodic part loses electrons and releases metal ions. Electrons move to the cathodic part outside the droplet, where oxygen and water react to form hydroxide ion. These hydroxide ions produced at cathode move inside the water droplet and react with metal ions at anode to form metal oxide. There are various ways to protect the substrate from corrosion. However, this work emphasizes on passive corrosion protection using polymeric coatings. Coatings containing anti-corrosive agents are applied on metallic surface to provide barrier in between the metallic surface and corrosive agents. Different types of anticorrosive agents are water-borne anticorrosive agents, solvent based anticorrosive agents, dipping waxes, and corrosion protective oils.

Reinhard et al. [2] studied the application of corrosion inhibitors in water-borne coatings. They used water-borne coatings for corrosion protection of mild steel instead of toxic organic solvents. They substituted mercapto compounds as corrosion inhibitors in acrylate- based dispersion. These mercapto compounds reduced early rusting during film formation without altering the properties of the acrylate dispersion. The acrylate-based dispersion was prepared by using copolymer of butyl esters of acrylic acid, styrene and methacrylic acid. It also contained acrylic acid, monoesters and polymerization initiator ammonium persulphate $(NH_4)_2S_2O_8$. Corrosion inhibitors present in acrylate dispersion were investigated by using a model electrolyte (0.03 M KNO_3 in double distilled water + 0.01 M acrylic acid). Using electrochemical impedance spectroscopy (EIS) that they found the anticorrosive property of mercapto compounds increased with the increase in pH values. EIS also showed that mercapto compounds were involved as a crosslinking agent during layer formation.

Perrin et al. [3] synthesized and characterized waterborne corrosion protection coating using poly(aniline) nanoparticles. They used aqueous amphiphile solution of phosphonic acid. Poly(aniline) dispersion was prepared in the presence of an oxidizing agent, ammonium peroxydisulphate (APS), and a surfactant, n-decylphosphonic acid (DPA). DPA acted as dopant anion. Energy dispersive X-ray spectroscopy revealed that when the surface of DPA doped poly(aniline) coating was scratched, then the dopant anion released to further protect the metal surface from corrosion. The surfactant concentration was kept higher than the critical micelle concentration (CMC) for the preparation of water/DPA solution. DPA has property to form vesicles in water and these vesicles coexited with vesicles of aniline and n-decylphosphonic acid. Precipitates of polyaniline were formed due to unstable reaction mixture. DPA to aniline molar ratio was kept greater than 1 in all poly(aniline) dispersions because at higher surfactant concentration no precipitates were obtained. Higher value of electrical conductivity was obtained at molar ratio 1.25 of APS/aniline. FT-IR analysis showed that poly(aniline) was doped efficiently with DPA. Thermo gravimetric analysis showed that DPA doped poly(aniline) had good thermal stability at least up to 260℃. The interlayer distance of poly(aniline) increased with higher concentration of DPA as shown by the DPA-poly(aniline) XRD analysis in emerlidine salt. This shows the effective penetration of the dopant.

Baskar et al. [4] synthesized poly((E)-(1-(5-(4-(3-(4-chlorophenyl)-3-oxoprop-1-enyl) phenoxy)decyl)-1H-1,2,3-triazol-4-yl)methyl acrylate) and poly((E)-(1-(5-(4-(3-(4-chloro-phenyl)-3-oxoprop-1-enyl)phenoxy) pentyl)-1H-1,2,3-triazol-4-yl) methyl acrylate), which are crosslinkable on photo irradiation. These polymers were coated on mild steel to protect it from corrosion in 1.0 M HCl solution. FT-IR analysis showed the presence of photosensitive chalcone moieties. The spectra given by H NMR results confirmed the formation of polymer. Crosslinking of polymer under the influence of photo illumination was confirmed by absorption spectroscopy. The morphology given by SEM analysis confirmed that these photo crosslinking polymers can protect mild steel from corrosion.

Pour-Ali et al. [5] suggested that direct addition of poly(aniline) particles in epoxy matrix resulted in aggregation of the particles. Thus, the polymer was synthesized using a different way. The epoxy matrix was modified using polyethylene glycol (PEG), and poly(aniline)-camphorsulphonate particles were prepared in the epoxy network. Mild steel was coated using this prepared polymeric coating in order to protect it from corrosion in 3.5% NaCl medium. The prepared characteristic description of polymeric coating was characterized by FT-IR and TEM. Anticorrosive nature of polymeric coating in 3.5% NaCl solution was determined using several techniques like EIS and salt spray test.

Baldissera and Ferreira [6] prepared different epoxy matrix (EM) based coatings by incorporating different forms of poly(aniline) (PANI). These coatings were utilized for protecting mild steel substrates from corrosion in 3.5% NaCl solution. Different forms of PANI like PANI-sulphonate, PANI-fibers, PANI-emerlidine salt, PANI-emerlidine base, PANI-zinc phosphate, PANI-zinc chromate were prepared. Different coatings prepared by incorporating these forms of PANI in epoxy matrix showed better anticorrosive nature as compared to simple epoxy coatings. Electrochemical impedance spectroscopy determined that the coating prepared by incorporating PANI-sulphonate in epoxy matrix showed more desirable anticorrosive behavior than other coatings.

Behzadnasab et al. [7] fabricated polymeric coatings for protection of mild steel from corrosion in 3.5% NaCl solution. Polymeric coatings were prepared using ZrO_2 nanoparticles, which were modified using amino propyl trimethoxy silane (APS). Further, these modified ZrO_2 particles were added in epoxy matrix. APS helped to form chemical bonds in between epoxy matrix and ZrO_2 particles and these particles got properly distributed in the epoxy matrix. The anticorrosive nature of the resulting polymeric coatings was enhanced at 2–3 wt. % of ZrO_2. The salt spray test and electrochemical independence spectroscopy were used to determine the corrosion resistance of polymeric coatings.

Kocijan et al. [8] studied the comparison and characterization of biocompatible polymer coatings on AISI316 L stainless steel. Biofouling reduces the efficiency of materials and contributes to corrosion of metals and alloys. Poly(dimethylsiloxane) PDMS and poly(ethylene glycol) (PEG) were used for surface modification of AISI316 L stainless steel. PDMS induced hydrophobic nature in the substrate by changing the surface wetting properties. PDMS has water contact angle greater than 90° and decreased the free energy of the surface. It acted like a water repellent and protected the surface from corrosion. On the other hand, the contact angle of PEG and water was less than 90° which induced hydrophilic nature to the system. The free energy of the substrate surface was also increased. PEG has anticorrosive properties, but less than PDMS. X-ray photoelectron spectroscopy determined that PEG coating was slightly thicker than PDMS. Their electrochemical impedance spectroscopy data confirmed that PDMS coatings applied on stainless steel has superior anticorrosion properties than PEG.

El-Mahdy et al. [9] prepared corrosion resistant coatings of magnetite/ acryl amide-co-sodium acrylate nano-composite and these coatings were tested on mild steel substrate in HCl solution. Preparation of nanocomposite coating was based on core-shell system. The magnetite nanoparticles were modified using NMA (polyoxyethylene 4-nonyl-2-propyl-phenyl/Maleic anhydride adducts). These magnetite/NMA nanoparticles were used as a core. The crosslinked acryl amide-co-sodium acrylate containing magnetite nanoparticles was used as shell. Transmission electron microscopy results confirmed that magnetite nanoparticles were dispersed inside the polymeric matrix in the presence of magnetite/NMA nanoparticles. The characteristic properties of coatings were investigated using UV-VIS spectroscopy and Fourier transform-infrared spectra.

Xu et al. [10] studied the facile fabrication of super hydrophobic polyaniline structures and their anticorrosive properties. They used different surfactants, that is, SDBS (sodium dodecylbenzene