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CORROSION PROTECTION OF STEELS: A BRIEF REVIEW ON CONDUCTIVE POLYMERS

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Abstract: The conventional anticorrosive coatings which are based on heavy metals such as chromium, zinc and copper are toxic to the environment. There has been a need to find suitable replacement coatings to be environmentally friendly and effective to inhibit corrosion of steels. Conductive polymers have acquired more attentions in the last years due to their environmentally benign nature and high effectiveness to protect steels against corrosion. Owing to their redox properties, conductive polymers can interact with the steels, forming a compact layer to protect the substrate surface against corrosion. Present brief review paper try to summarize study on conductive polymers and their anticorrosive properties. The following concepts are discussed sequentially in this paper: corrosion protection using conductive polymers and conductive polymer applying methods on steels.

Key words: conductive polymer, corrosion, anticorrosive coating.

1. INTRODUCTION

Traditionally, polymers were used as insulator which restricts the flow of electrons and functioned as electrical barrier in industry. In 1977 with discovery of doped-polyacetylen, by Shirakawa et al, the new term of conductive polymer was borned. In the year 2000, they acquired the Nobel Prize in chemistry for discovery and progress of conductive polymers [1-2]. Conductive polymers possess unique chemical structure which consists of conjugated chains containing π-electrons delocalized alongside the polymer. The repositioning of electrons within this π-framework is the cause of conductivity [3]. Conductive polymers have gained more attentions in different applications where electrical conductivity is needed. Batteries, transistors, sensors, electrochromic displays, light-emitting diodes, capacitors and corrosion protection coatings are potential application areas of conductive polymers [4-12]. One of the applications of conductive polymers is corrosion protection of steels. The bad performance and environmental toxicity of conventional coatings persuade scientists to find a proper replacement coating to combat corrosion.

Corrosion protection applying conductive polymers was first proposed by MacDiarmid in 1985. The interest in using conductive polymers as anti-corrosive coating has risen up with the time due to their effectiveness and environmentally friendly nature. The conductive polymers could interact with the steel and form a compact layer to inhibit a corrosion process. When conductive polymers are used as anti-corrosive coatings, some points have to be considered to inhibit corrosion effectively. These points include on how to apply conductive polymers on steels, conductive polymers electrical conductivity, conductive polymers environmental stability, conductive polymers pocessability, and ease of synthesis of conductive polymers. Based on the aforementioned factors there are several conductive polymers including polyaniline, polypyrrole, polyacetylene, polythiophene, polyparaphenylene which could act effectively to inhibit corrosion. The chemical structures of some conductive polymers are shown in Figure 1[2, 13].

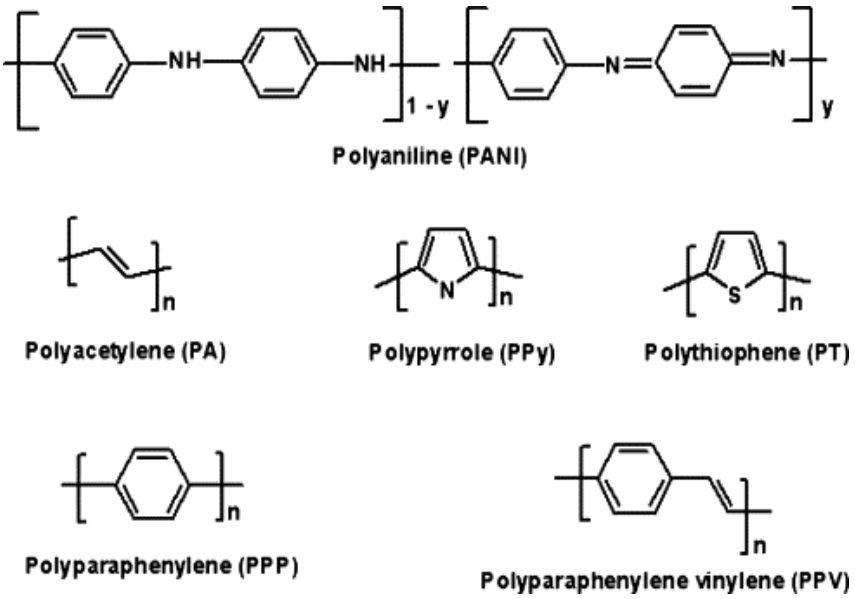


Figure 1. The structure of some conducting polymers [2].

Among these polymers, polyaniline has been widely studied due to its low cost, ease of synthesis, high conductivity, environmental stability and redox properties [14, 15]. Several studies have been done to investigate on anticorrosion performance of conductive polymers. Elaine Armelin et al (2008) have used polyaniline and polypyrroel contained coatings to protect steel against corrosion [4]. Toshiaki Ohtsuka (2012) has well reviewed on corrosion protection of steels using polypyrrole coating [22]. G.S. Goncalves et al (2011) have studied on anticorrosion properties of alkyd coatings containing polyaniline. M.A. Lucio Garcıa et al (2006) have electroplated polypyrrole coating to protect stainless steel against corrosion [23]. P. A. Cook et al (2004) and Roberto M. Torresi et al (2005) have well described the mechanism of protection of steels using conductive polymers [24-25].

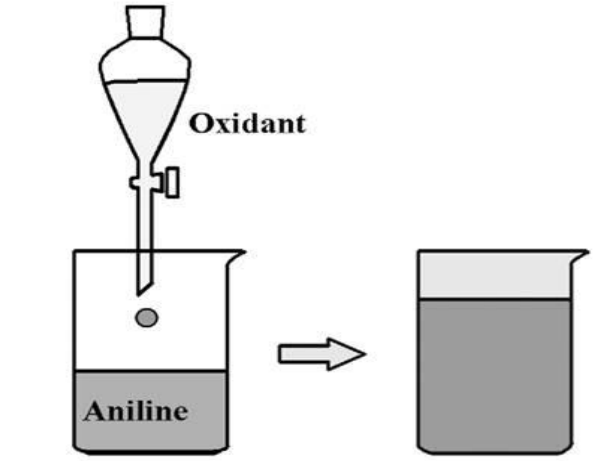
This review paper presents a brief view on the corrosion protection of steels using conductive polymers. It begins with describing the synthesis methods of conductive polymers, briefly discussing on conventional electrochemical and chemical synthesis methods. It continues on describing the anti-corrosion mechanism of conductive polymers which is proposed and investigated in several studies [24-25]. At the end it introduces the best method for application of conductive polymer on steel substrate to effectively inhibit corrosion. Based on our literature this review paper is the first that briefly discussed on the significance of synthesis and applying methods which affect the anti-corrosion performance of conductive polymers.

2. SYNTHESIZE METHODS OF CONDUCTIVE POLYMERS

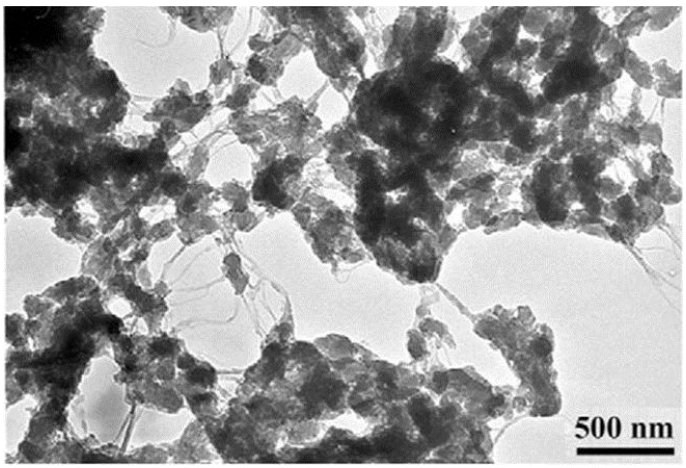
There are normally two common methods for synthesise of conductive polymers: 1) chemically and 2) electrochemically. Each of these methods has its own advantages.

2.1. Chemical method

In the chemically synthesise method, the monomer oxidation is performed using oxidizing agent in an acidic aqueous medium and polymer is obtained as a precipitate [16]. The schematically chemically synthesize of conductive polymers (polyaniline) followed by an SEM image of chemically synthesized conductive polymers (polyanilne) is shown in figure 2 [17].



(a)



(b)

Figure 2: a) Schematic of chemical synthesis of polyaniline. The oxidative polymerization reaction of aniline is typically carried out in an acidic solution (e.g., 1 M HCl) . b) SEM image of polyaniline [17]

Chemical methods are normally used for synthesis of conductive polymers in bulk quantities which is important for practical reasons. Based on the shape and size of polymer, chemical polymerization could be subdivided further into: heterophase, solution, interfacial, seeding, metathesis, self-assembling, and sonochemical polymerizations. The normal chemical synthesis method gives partially micro-sized PANI particles as shown in Figure 2(b).

2.2. Electrochemical method

Electrochemical methods can be used for synthesizing the conductive polymers. Anodic oxidation of the monomer at electrode is a simple illustration of this method. Potentiostatic or galvaniostatic are common techniques used for electrochemical synthesizing of conductive polymers, which is shown in figure 3[19].

In electropolymerzation process some parameters such as applied current density, deposition time, and monomer concentration could influence on the polymer. It has been found that the polymer coating surface became rougher either by increasing the monomer concentration or increasing the deposition time [19]. Figures 4 and 5 reveal the change in polymer roughness by increasing the monomer concentration and deposition time [19].

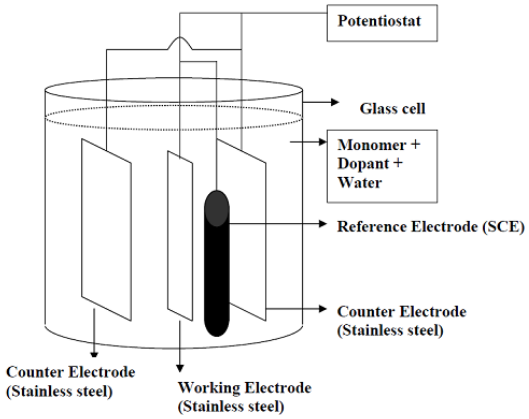


Figure 3: Schematic of Potentiostat/Galvanostat setup [19]

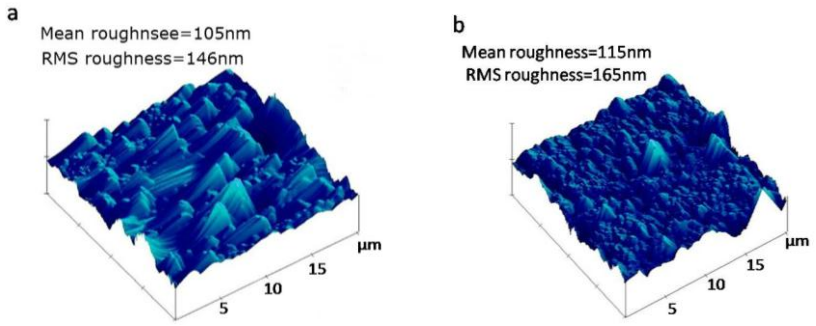


Figure 4. AFM images of polypyrrole coating on stainless steel at **a**) 0.1 M pyrrole **b**) 0.2 M pyrrole, at 2 minutes deposition [19].

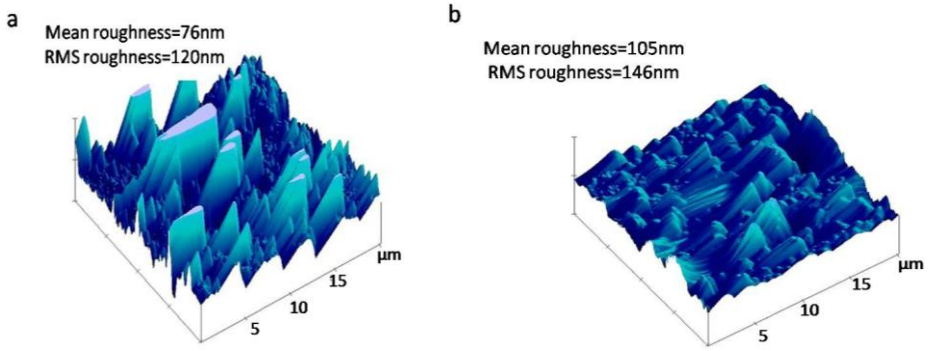


Figure 5. AFM images of polypyrrole coatings on stainless steel at a) 30 seconds, b) 2 minute deposition time, at 0.1 M pyrrole [19]

The advantages of electrochemically synthesize methods are including: 1) No need to use oxidizing agents 2) Ability to dope the polymer with different ions, 3) the electrochemically synthesized polymer has better adherence in comparison with chemically synthesized polymers and also 4) The thickness and morphology of conductive polymers film could easily be controlled [19].

3. CORROSION PROTECTION USING CONDUCTIVE POLYMERS

Conductive polymers have been extensively applied for corrosion protection purposes. Environmentally friendly nature and high effectiveness lead conductive polymers to become as a proper replacement of conventional coatings to combat corrosion in different environments. Corrosion protection using conductive polymers was first suggested by Macdiarmid in 1985. Due to their redox properties conductive polymers could interact with the metal substrate and form a layer to inhibit corrosion process.

Several proposed mechanisms of corrosion protection using conductive polymers are: (a) They could lead to the formation of an electric field on the metal surface, hindering the flow of electrons from metal to oxidant; (b) They could act as barrier coating by forming a dense, strong adherent and low-porosity film on the metal surface. (c)In presence of conductive polymers the metal could form a protective oxide layer on its surface [16, 20 and 21].

The proposed protection mechanisms are numerous especially for polyaniline and polypyrrole, but the most accepted is the self-healing provided by conducting polymers, which is a combination of electrical barrier and cathodic protection systems.

There are different methods to apply conductive polymers on the metal: (i) as a coating alone (ii) as an additive to modify the conventional organic coating [2].

3.1. Conductive polymers as coating alone

Electrodepositing of conductive polymers on the metal is the first method used by the industries. However deposition of conductive polymers alone on the metal surface sometimes has poor performance. One reason is the high porosity of conductive polymers. Through the porosity the chloride ions, water and O_2 could easily penetrate and touch the bare metal which at last cause corrosion of the metal. The modified methods were suggested for conductive polymers to have better performance against corrosion process [12-15].

3.2. Conductive polymers as additive to modify conventional coatings

Another method for applying conductive polymers on the metal substrate is using conductive polymers as additive in the conventional coatings to modify their anti-corrosive properties. One of the important factors lead to better performance of this coating is the homogeneous distribution of conductive polymers in the coating material. However the miscibility of conductive polymers (PANI) in the paint is a determinant factor. In order to obtain the homogeneous dispersion of conductive polymers inside of paint, one strategy is to incorporation of the substituent facilitating the solubility of the conductive polymers in the paint, producing a homogenous conductive polymers modified paint. One of the most interesting features is that by using very low concentration of conductive polymers the effective anticorrosive properties could be obtained. The low concentration (0.2-0.3wt %) of conductive polymers additive does not lower the adherence of the paint to metal substrate. The mechanism of corrosion protection of conductive polymers modified coating consists of electrochemical and barrier protections. Electrochemical protection is as a result of the presence of conductive polymers and the barrier protection is due to matrix paint. Due to good performance of using conductive polymers as additives in the conventional coating it become one of the most promising approach in corrosion protection coatings area. [19-21].

4. CONCLUSIONS

a) Conductive polymers have extensively been found as a proper replacement of conventional coatings because of their good effectiveness and also environmentally friendly nature. The mechanisms which conductive polymers could have anticorrosive behavior are: (a) Conductive polymers lead to formation of an electric field on the metal surface, hindering the flow of electrons from metal to

oxidant; (b) Conductive polymers could act as barrier coating by forming a dense, strong adherent and low-porosity film on the metal surface. (c)In presence of conductive polymers, the metal could form a protective oxide layer on its surface.

b) Two methods commonly used for synthesizing of conductive polymers are chemical methods and electrochemical methods, where chemical method is suitable for large quantities of compounds and electrochemical method is suitable for getting a high quality coating with control on its thickness.

c) The most effective method of applying of conductive polymers on the metal is to use it as an additive to modify the conventional organic coatings. The advantage of this method is that a low concentration of anticorrosive additive is required.

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