CONDUCTIVE POLYMER COATINGS TOWARDS INHIBITION OF MICROBIAL-INDUCED CORROSION OF LOW CARBON STEEL

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To:

My beloved family

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ABSTRACT

Microbial-induced corrosion (MIC) is an electrochemical form of corrosion that is initiated, facilitated, or accelerated by bacteria and biofilms on the metal substrate. Coating methods have been widely used to inhibit MIC because of their effectiveness, ease of application and low cost. Conventional coatings for MIC inhibition are based on heavy metals such as tin, copper, and zinc; however, these coatings are toxic to the environment. Recently, environmentally friendly coatings were developed to overcome MIC problems. Among these new coatings, studies have focused on conductive polymers, which have both antibacterial and anticorrosive properties. The biocidal and anticorrosive properties of conductive polymers make them appropriate coatings for MIC inhibition. This research project is aimed to study and compare the behaviour towards MIC of four types of conductive polymer coatings namely, polyaniline nanofibres, polyaniline-silver nanocomposite, polyaniline-carbon nanotube, and polyaniline-graphene nanocomposite. These polymers were synthesized and produced through *in situ* chemical polymerization from various chemicals. This was followed by coating the synthesized polymer coatings onto mild steel substrates by solvent casting method. The behaviour of the polymer coated substrates towards MIC was investigated through immersion test in *Pseudomonas aeruginosa* inoculated nutrient-rich simulated seawater (NRSS) medium for one to eight weeks. The corrosion rates and corrosion resistance of the coated mild steel were determined by electrochemical test and electrochemical impedance spectroscopy (EIS) in 3.5% sodium chloride solution respectively. Materials characterisation and analysis were carried using field emission electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Adhesion and conductivity test were performed on the polymer-coated mild steels using pull off and four point probe instruments respectively. The overall results show that nanocomposite coatings displayed better MIC inhibition behavior in comparison with pure polyaniline coating and PANI-graphene act as the best MIC inhibition coating. This is due to the good antibacterial and anticorrosive properties of the coating which effectively inhibit MIC. In addition, electrically conductive polymer coatings could inhibit biofilm formation and impart good anticorrosive properties. This research project concluded that these conductive polymer coatings are suitable candidates for MIC inhibition applications.

ABSTRAK

Kakisan dipengaruhi mikrob (MIC) adalah satu bentuk elektrokimia kakisan yang dimulakan, dipermudahkan, atau dipercepatkan oleh bakteria dan biofilem pada substrat logam. Kaedah salutan telah digunakan secara meluas untuk merencat MIC kerana keberkesanannya, mudah digunakan dan kos yang rendah. Salutan konvensional untuk perencatan MIC adalah berdasarkan kepada logam berat seperti timah, kuprum, dan zink. Walau bagaimanapun, salutan ini adalah toksik kepada alam sekitar. Baru-baru ini, salutan mesra alam telah dibangunkan untuk menyelesaikan masalah MIC ini. Di kalangan salutan baru tersebut, kajian telah memberi tumpuan kepada polimer konduktif, yang mempunyai kedua-dua sifat antibakteria dan antikakisan. Polimer konduktif sesuai digunakan sebagai salutan untuk merencat MIC kerana mempunyai sifat biosidal dan antikakisan. Projek penyelidikan ini bertujuan untuk mengkaji dan membandingkan kelakuan terhadap MIC empat jenis salutan polimer konduktif iaitu nanogentian polyanilina, nanokomposit polyanilina-perak, polyanilina-nanotiub karbon, dan nanokomposit polyanilina-graphena. Polimer ini disintesis dan dihasilkan melalui pempolimeran kimia *in situ* daripada pelbagai bahan kimia. Ini diikuti dengan menyalut salutan polimer yang telah disintesis ke atas substrat keluli lembut dengan menggunakan kaedah tuangan pelarut. Kelakuan substrat tersalut polimer terhadap MIC telah dikaji melalui ujian rendaman dalam larutan *Pseudomonas aeruginosa* disuntik yang kaya dengan nutrien air laut simulasi (NRSS) selama satu hingga lapan minggu. Kadar kakisan dan ketahanan kakisan keluli lembut tersalut ditentukan melalui masing-masing ujian elektrokimia dan spectroskopi impedans elektrokimia (EIS) dalam larutan natrium klorida 3.5%. Pencirian bahan dan analisis dilakukan dengan menggunakan medan pancaran mikroskop elektron imbasan (FESEM), tenaga-serakan sinar-x spektroskopi (EDS), jelmaan Fourier spektroskopi inframerah (FTIR), pembelauan sinar-x(XRD) dan mikroskopi elektron transmisi (TEM). Ujian rekatan dan konduktivi telah dilaksanakan ke atas keluli lembut tersalut polimer dengan menggunakan masing-masing alat perengang dan alat empat mata kuar. Keputusan kajian secara keseluruhan menunjukkan bahawa salutan nanokomposit menghasilkan kelakuan antikakisan lebih baik jika dibandingkan dengan salutan polyanilina tulen. Ini disebabkan aktiviti biosidal kumpulan nitro bercas positif dalam rantai molekulnya. Dengan lain perkataan, salutan konduktif elektrik boleh merencat pembentukan biofilem dan memberi sifat antikakisan yang baik. Projek penyelidikan ini merumuskan bahawa salutan polimer konduktif mesra alam sekitar sesuai sebagai calon aplikasi untuk perencatan MIC.

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LIST OF ABBREVIATIONS

Al	-	Aluminum
AA	-	Aluminum alloy
Ag	-	Silver
ATRP	-	Atom transfer radical polymerisation
BT	-	2, 2′-Bithiophene
CTS	-	4-(chloromethyl)-phenyl tricholorosilane
Cu	-	Copper
DNA	-	Deoxyribonucleic acid
EPS	-	Extracellular polymeric substances
E	-	Elastic modulus
E_{corr}	-	Corrosion potential
FM	-	Fluorescence microscope
G	-	Grafted
I_{corr}	-	Corrosion current density
IOB	-	Iron oxidizing bacteria
IRB	-	Iron reducing bacteria
LB	-	Lysogeny broth
MIC	-	Microbial-Induced Corrosion
MOB	-	Manganese oxidizing bacteria
MS	-	Mild steel
N^+	-	Positively charged nitrogroups
NPs	-	Nanoparticles
NPVP	-	Poly (4- vinylpyridine)-co-poly (4-vinyl-N- hexylpyridinium bromide)
PANI	-	Polyaniline

PBT	-	Poly (2, 2′-Bithiophene)
PDA	-	Poly (dopamine)
P (DMEMA)	-	Poly (2-dimethylaminoethyl methacrylate)
PDMS	-	Poly (dimethylsiloxane)
P (GMA)	-	Poly (Glycidyl Methacrylate)
PMOX	-	Poly (2-methyl-2-oxazoline)
PEG	-	Poly (ethylene glycol)
PEO	-	Polyethylene oxide
PFPEs	-	Perfluoropolyethers
P (GMAA)	-	Poly (glacial methacrylic acid)
PMOX	-	Poly (2-methyl-2-oxazoline)
PNMA	-	Poly N-methylaniline
PoPD	-	Poly (o-phenyldiamine)
PPA	-	Polyphthalamide
PPy	-	Polypyrrole
PTFE	-	Polytetrafluoroethylene
P (4-VP)	-	Poly (4-vinylpyridine)
PVAn	-	Poly (vinyl-aniline)
Q	-	Quternised
QASs	-	Quaternary ammonium salts
SI-ATRP	-	Surface initiated atom transfer radical polymerisation
SOM	-	Surface oxidized metal
SSMB	-	Simulated seawater-based. Modified Baar's
SRB	-	Sulphate reducing bacteria
SIP	-	Surface initiated polymerisation
SS	-	Stainless steel
SAM	-	Self-assembled monolayer
SEM	-	Scanning electron microscopy
TBT	-	Tributyltin
TMSPMA	-	3-(Trimethoxysilyl) propyl methacrylate
Ti	-	Titanium

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Microbial-Induced Corrosion (MIC) is a destructive type of corrosion, which is initiated, facilitated or accelerated due to presence and activity of bacteria [1, 2] and mostly appears in the form of localized pits and crevices on metal surfaces [3]. The bacteria tend to attach to a substrate, and form a biofilm layer where it creates a condition that accelerates corrosion. The bacteria in the biofilm state tend to accelerate and facilitate the corrosion and cause severe damage to the metal [4-7].

One group of metal alloys that are less resistant to MIC are steels, which includes carbon steels such as mild steel [8-12] and stainless steel [3, 13 and 14]. These metals are mostly used in marine industries because of their good mechanical properties and relatively less cost. However, their common limitation is that they are not immune to MIC. Generally, steels are susceptible to MIC as shown by their chemical reaction with different types of bacteria such as iron reducing bacteria [11], sulfate-reducing bacteria, iron-oxidizing bacteria [3], manganese oxidizing bacteria [15] and slime former bacteria [16]. These bacteria cause localized pitting or crevice corrosion on the steel surface through the formation of biofilms and further colonization by other bacterial types.

Pseodomonas aeruginosa is a dominant bacterium in marine environments, and one of the aerobic slime former bacteria, which forms a biofilm layer on the steel surface. The chemical reaction of biofilm layer with the steel and the formation of differential aeration cells create conditions on steel, which initiate and accelerate the corrosion process. The generation of these concentration cells is detrimental to the integrity of the oxide layer and enhances the susceptibility of steels to corrosion [17-19].

To overcome MIC, different methods such as biocide treatment, cathodic protection and coatings have been used [20-24]. Coatings are widely used because of their ease of application, effectiveness, and low cost [22, 23]. To inhibit MIC, coatings must have antibacterial and anticorrosive properties. Conventional MIC-inhibition coatings are based on heavy metals such as tin, copper and zinc. This type of coating can protect substrates against MIC; however, these coatings are toxic to the environment and are carcinogenic to humans [25].

Recent studies have examined the use of environment-friendly coatings for MIC-inhibition [23]. Environmentally friendly conductive polymers were discovered recently; these polymers are suitable for MIC inhibition because of their anticorrosive and antibacterial properties [26]. The high redox properties of conductive polymers can passivate steel, generating a protective oxide layer. Due to their positively charged nitro-groups, conductive polymers display biocidal properties, inhibiting bacterial attachment and biofilm formation [26]. This project aims to study on MIC process of steels and the application of environmentally friendly conductive polymer coatings to inhibit MIC.

1.2 Problem Statement

There are generally three main strategies for MIC inhibition coatings: a) biocide leaching, b) adhesion resistance and c) contact killing. Conventional coatings are based on heavy metals such as copper, zinc, chromium and tin that inhibits MIC through biocide leaching. These coatings are toxic to the environment and have cancerous effects on human body. The adhesion resistance is not an effective strategy to inhibit MIC. The contact killing strategy is favorable and polycationic coatings are used to inhibit MIC through this strategy. Although polycationic coating display biocide activity however their corrosion resistance properties are poor. There is a need to find environmentally friendly coatings to inhibit MIC effectively. Due to their biocide behavior and anticorrosive properties environmentally friendly conductive polymers are good candidate to protect metal surfaces against MIC.

1.3 Purpose of the Research

The purpose of this research is to investigate on environmentally friendly coatings for MIC inhibition applications. First, the research induces an investigation on the mechanisms of MIC behavior of steel in bacteria inoculated medium. This could be useful to enable application of efficient mitigation programs to inhibit MIC of steel. Second, the research induces an investigation on the MIC inhibition properties of conductive polymers. The output of this research is expected to improve the MIC inhibition properties of coated steels exposed to bacteria inoculated medium. This study is expected to provide the good candidate MIC inhibition coatings with are effective and also have an environmentally friendly nature.

1.4 Objectives of the Research

The objectives of the research are as follows:

1. To develop conductive polymers which can be used as coating materials to inhibit microbial-induced corrosion.

2. To determine the microstructure and properties of the conductive polymers coated on the carbon steel.

3. To determine the performance of the conductive polymers as coatings material inhibiting microbial-induced corrosion.

4. To propose a mechanism of conductive polymer coating to inhibit microbial-induced corrosion.

1.5 Scopes of the Research

The scope of the research is as follows:

1. Synthesis of polyaniline, polyaniline-silver nanocomposite, polyaniline-carbon nanotube nanocomposite and polyaniline-graphene nanocompsoite through *in situ* chemical polymerisation method.

2. Characterisation of the synthesised polymer powders, uncoated and coated substrates: using various techniques namely, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR),

Energy Dispersive Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), Four Point Probe, Electrochemical Tafel Analysis and Electrochemcial Impedance Spectroscopy (EIS).

3. Preparation of *P. aeruginosa* bacteria inoculated medium for immersion test.

4. Perform immersion test at varying immersion time.

5. Analysis of samples after immersion test using the standard characterisation equipment.

1.6 Significance of the Research

The basic aim of this research is to provide significant information on the microbial-induced corrosion (MIC) inhibition behavior of conductive polymer coated steel exposed to bacteria inoculated medium. Thus, the results of this research will benefit the many industries, especially in maritime, oil and gas fields.

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