

EVALUATION OF POLYANILINE COMPOSITES AND NANOSTRUCTURES  
AS ANTI-CORROSIVE PIGMENTS FOR CARBON STEEL

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Thesis submitted in fulfillment of the  
Requirements for the award of the degree of  
Master of Engineering (Polymer)

Faculty of Chemical and Natural Resources Engineering  
Universiti Teknologi Malaysia

APRIL 2010

*To ALLAH, I hope the approval and acceptance for this work*

*To the cradle of civilizations my country, IRAQ*

*To the real meaning of fatherhood, my father*

*To paradigm of sacrifice, my mother*

*To my love, my wife*

*To my next big hope, my son*

## ACKNOWLEDGEMENTS

Firstly I would like to thank ALLAH and admit: We are not aware of any knowledge except what it has taught us, you are the most knowing and the wisest

I thank all people who have taught me and helped me to do this work especially grateful to my supervisors Dr. Mohammed Ilyas Khan and Assoc. Prof. Dr. Shahrir Hashim for their support, advice and guidance given to me through my work. Also would like to appreciate the financial support from Research Management Centre at University of Technology Malaysia through grant number 77511 was highly significant.

## ABSTRACT

Conducting polymers have recently been studied as a new class of materials for the corrosion protection of metals. Polyaniline (PANI) is the best candidate to perform this function due to its high environmental stability and simple preparation. Polyaniline was synthesized by polymerizing aniline monomer with various inorganic oxides and with several ratios of phosphoric acid doping. The prepared samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction Meter (XRD) and the morphology of these samples was examined using Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM). Electrical conductivity of the samples was measured using a multimeter. Besides, pigments dispersion stability was observed in ethanol medium at six increasing times (0, 1, 3, 6, 12 and 24 hours). The prepared samples were used as anti-corrosive pigments by blending with commercially available acrylic paint. The blended pigments and acrylic paint were then applied on carbon steel panels by simple dip coating method. The coated steel panels were then dried at room temperature for two days. Once the coatings were fully dried, the steel panels were immersed in 5% NaCl solution for 60 days and left in salt spray chamber for 35 days according to standard ASTM G31 and ASTM B117 respectively. The degree of corrosion for full immersion test samples were evaluated by calculating the corrosion rate from weight loss method and by visual observation for samples exposed in salt fog chamber. The adhesion strength was measured according to ASTM D3359 standard. Sample that was most affected by corrosion, has lower adhesion strength with metal. The degrees of corrosion on the steel panel are related to the pigment used in paint and thus the best PANI composite pigment for corrosion protection was PANI-Silicone dioxide (PANI-SiO<sub>2</sub>) while the best nano form in terms of corrosion protection was PANI nanofiber. This was due to its highest electrical conductivity and good adhesion strength for PANI-SiO<sub>2</sub> and better dispersion stability for PANI nanofibers.

## ABSTRAK

Polimer berkonduktif yang telah dikaji merupakan sejenis bahan baru untuk perlindungan kakisan logam. Polianilina (PANI) adalah polimer terbaik untuk tujuan ini kerana mempunyai kestabilan persekitaran yang tinggi dan proses penyediaannya yang mudah. Polianilina dengan pelbagai jenis oksida tak organik serta beberapa nisbah asid fosforik telah disintesis melalui proses pemolimeran dari monomer analina. Sampel-sampel yang telah siap disintesis telah dicirikan dengan menggunakan Spektroskopi Infra-merah Transformasi Fourier (FTIR) dan Pembelauan Sinar-X (XRD), manakala morfologi sampel-sampel ini dikaji dengan menggunakan Microskopi Imbasan Elektron (SEM) dan juga Microskopi Imbasan Elektron Pemancaran Medan (FESEM). Konduktiviti elektrik sampel-sampel ini diukur dengan menggunakan multimeter. Kestabilan penyebaran pigmen ini di dalam media etanol diperhatikan sebanyak enam masa berbeza yang meningkat (0, 1, 3, 6, 12 dan 24 jam). Sampel-sampel yang telah disediakan akan digunakan sebagai pigmen anti-kakisan secara mengadunnya dengan cat akrilik komersil yang sedia ada. Pigmen yang telah diadunkan ke dalam cat akrilik tadi kemudiannya akan disaluti ke atas besi karbon berpanel secara kaedah lapisan celup mudah. Besi karbon berpanel yang telah disaluti kemudian dikeringkan pada suhu bilik selama dua hari. Setelah lapisan cat kering sepenuhnya, besi karbon berpanel tersebut direndam di dalam larutan NaCl 5% selama 60 hari dan juga di dalam ruang semburan garam selama 35 hari mengikut piawaian ASTM G31 dan ASTM B117. Darjah kakisan untuk sampel-sampel yang menjalani ujian pencelupan sepenuhnya dikira secara pengiraan kadar kakisan dari kaedah pengurangan berat, manakala darjah kakisan untuk sampel-sampel yang telah didedah di dalam ruangan semburan garam akan dinilai melalui pengamatan visual kemudian kekuatan pelekatannya dinilai mengikut piawai ASTM D3359. Sampel yang mengalami kakisan yang tinggi adalah sampel yang mempunyai kekuatan pelekatan besi yang rendah. Darjah kakisan pada besi berpanel adalah berkait rapat dengan jenis pigmen yang telah digunakan di dalam cat, oleh itu pigmen komposit PANI yang terbaik untuk perlindungan kakisan adalah PANI-Silikon dioksida (PANI-SiO<sub>2</sub>), manakala perlindungan kakisan dalam bentuk nano yang terbaik adalah PANI berserat nano. Ini disebabkan oleh konduktiviti elektrik yang tertinggi dan kekuatan pelekatan yang baik untuk PANI-SiO<sub>2</sub> dan kestabilan penyebaran yang baik untuk PANI berserat nano.

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**LIST OF ABBREVIATION/ SYMBOLS**

PANI	Polyaniline
PPY	Polypyrrole
PIC	Polyaniline Inorganic Composite
APS	Ammonium per sulfate
PTC	Polyaniline-TiO <sub>2</sub> composite
PFC	Polyaniline-Fe <sub>2</sub> O <sub>3</sub> composite
ATMP	Amino tri methylene phosphoric
GF	Glass flak
PGFC	Polyaniline glass flak composite
NaCl	Sodium chloride
HCl	Hydrochloric acid
H <sub>3</sub> PO <sub>4</sub>	Ortho-Phosphoric acid
EB	Emeraldine base
ES	Emeraldine salt
LB	Leucoemeradine base
MS	Mild steel
SS	Stainless steel
CS	Carbon steel

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. They were utilized as inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymer known as intrinsically conductive polymer or electroactive polymers are being discovered. Although this class is in its infancy, much like the plastic industry was in the 30's and 50's, the potential uses of these are quite significant.

Intrinsically conductive polymers (ICPs) are a new class of polymeric materials that are continuously exploited for a wide range of novel application including corrosion protection.

This discovery was published by Shirakawa in 1977 received the 2000 Nobel Prize in Chemistry for her study on ICPs reflecting the world's recognition of the unique characteristics and properties of these polymers and their promising technological applications.

It is the property of unsaturated polymers (conjugated) that they have an  $\sigma$ -bond spinal column of overlapping  $sp^2$  fusion orbitals. The residual out-of-plane Pz orbitals on the carbon atoms overlies with adjacent Pz orbitals to give  $\pi$ -bonds (Pi bonds). Also conjugated polymers have a skeleton of irregular single and double carbon-carbon bonds. The electrons that form the  $\pi$ -bonds are delocalized over the whole molecule and free to move along the polymer backbone. If the consecutive carbon atoms in a chain connect in  $\pi$ -bonding, the structure is supposed to be conjugated (Terje and John 2007).

### **1.1.1 Polyaniline in Corrosion Protection**

Over the past decade, published evidence that CPs, specifically polyaniline could inhibit corrosion has come from DeBerry (1985), Ahmad and MacDiarmid (1987). These results showed that PANI electrodeposited on passivated steel in a strong acid environment enhanced corrosion protection of the metal. While there is general agreement that PANI performs well in retarding corrosion on carbon steel, the mechanism for this process is still under investigation. Several hypotheses have been suggested for the mechanism of corrosion protection using CPs, specifically PANI:

- (a) PANI contributes to the formation of an electric field at the metal surface, restricting the flow of electrons from metal to oxidant.
- (b) PANI forms a dense, strong adherent, low-porosity film similar to a barrier coating;
- (c) PANI causes the formation of protective layers of metal oxides on a metal surface (McAndrew, 1997).

Organic coatings are an efficient way to protect metal-based products from corrosion. However, over the time even in the absence of defects a sufficient amount of ions may penetrate through the coating so that corrosion at the interface may occur.

But more dangerous are defects in the coating. Such defects may be caused by external attack of Aggressive ions, such as through impact by stones or scratches, or by production steps. In order to limit corrosive attack, corrosion inhibiting pigments are added to the paints and other organic coatings applied on metallic surfaces. The organic coatings can develop what is called “under coating corrosion” which starts from weak spots and develops into blisters and pitting leading to corrosion. Organic protective coating (barrier coating), therefore, fail by separation at the coating/substrate interface (Frankel, 1998).

This separation process is known as “delamination”, which leads in time to complete loss of the barrier properties of the coating. Several metal pretreatments have been developed to extend the lifetimes of organic coatings. These pretreatments are normally composed of phosphates, chromates and oxides, which contain a variety of metal cations. The most efficient pigments are those containing chromates (usually in form of strontium chromate), But because of their toxic and carcinogenic nature their use has to be progressively decreased and this material is a known human carcinogen (Blasiak and Kowalik, 2000)



In recent years it has been shown that intrinsically conducting polymers such as Polyaniline used effectively as pigment due to its environmentally friendly, anticorrosion ability, ease of preparation, excellent environmental stability and interesting redox properties associated with the chain of nitrogen. PANI incorporated conventional paint coatings (Acrylic) are able to protect steel due to their passivating ability. Up to now, only little is known about how corrosion protection by conducting polymers might work.

As nearly all studies focus on redox active conducting polymers, such as Polyaniline, Polypyrrole or Polythiophene, in the following ICP refers to redox active polymers only. A number of different mechanisms are proposed, such as the so-called “ennobling mechanism”, which is based on the assumption that conductive redox polymers such as polyaniline or polypyrrole, applied in their oxidized state.

## **1.2 Problem Statement**

One of the most serious problems that is faced by mankind is the corrosion. Corrosion naturally impacts our daily life through chemical reactions that occur between a metal or metal alloys and its environment because metal turns to return to their more stable, oxidized state. Corrosion occurs with both industrial, domestic environment and the corrosion of metal surface increases significantly as the structure ages. Corrosion should be prevented by the safest and lowest cost method during the earliest stage of corrosion through the use of conductive polymer. Conductive polymers are a new class of polymeric materials that are continuously exploited for a wide range of novel application including corrosion protection.

In recent years, it has been shown that electrically conducting polymers especially polyaniline incorporated conventional paint coatings are able to protect steel due to their passivating ability (Armelin *et al.*, 2008).

Conductive polymer applies for corrosion inhibitor either as first layer coated metal under conventional coating or blended with conventional coating. These blends are more widely used method due to; ease of preparation, excellent environmental stability and their pigment are distributed in each and everywhere in organic coating. Polyaniline (PANI) is recognized to be the best candidate for enhancing anticorrosion paint. This is because of simple synthesizing method, excellent environmental stability and having the best interesting redox properties associated with the chain of nitrogen among conductive polymers.

For the best of the authors' knowledge, the application of using the PANI composite with ( $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) and PANI with various nanoforms as pigments for corrosion protection has not been reported before; which is the major objective of this research. The use of such pigments is thought to enhance the efficiency of the coatings. This study describes the process of synthesizing and characterizing PANI with three various nanoforms and three different composites and then evaluating their anticorrosion performance using full immersion and salt spray tests carried out in acid media.

### **1.3 Research Objectives**

The objective of this research is to assess the anticorrosion properties of PANI and PANI Composites (PIC) in Acrylic paint as coating for carbon steel.

- i. To synthesise and characterize PANI in various nanoforms from different Monomer-Doping ratios of (Aniline-phosphoric acid) and use it as anticorrosion pigments.
- ii. To synthesise and characterize three PANI composites pigment (PANI-TiO<sub>2</sub>, PANI-SiO<sub>2</sub> and PANI-Al<sub>2</sub>O<sub>3</sub>) and use it as anticorrosion pigments.
- iii. To determine the effect of these synthesised pigments in acrylic paint for corrosion protection on carbon steel.

#### **1.4 Scope of Research**

- i. Synthesis four PANI from deferent phosphoric acid dopant ratios with 1M aniline monomer (1:0.1, 1:0.5, 1:1 and 1:2) and use them as pigments.
- ii. Synthesis three PANI composites pigment (PANI-TiO<sub>2</sub>, PANI-SiO<sub>2</sub> and PANI-Al<sub>2</sub>O<sub>3</sub>).
- iii. Characterization of the seven pigments using FTIR and XRD.
- iv. Observe of pigments morphology using SEM and FE-SEM.
- v. Study the pigments conductivity and the dispersion stability.
- vi. Blend these seven samples with Acrylic paint then applied on carbon steel samples.
- vii. Corrosion study for samples coated by salt spray fog chamber and fully immersion test of these samples according to standards ASTM B117 and ASTM G31 respectively.
- viii. Measuring coating thickness and study adhesion for samples according to standards ASTM D 1186 and ASTM D3359 respectively.