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ABSTRACT

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

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_2) 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_2 and better dispersion stability for PANI nanofibers.

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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 pempolimeran 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-$SiO2$), 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-$SiO2$ 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_2 composite PFC
	Polyaniline-Fe_2O_3 composite
ATMP	Amino tri methylene phosphoric
GF	Glass flak
PGFC	Polyaniline glass flak composite
NaCl	Sodium chloride HCl
	Hydrochloric acid
H_3PO_4	Ortho-Phosphoric acid
EB	Emeraldine base
ES	Emeraldine salt
LB	Leucoemeradine base
MS	Mild steel
SS	Stainless steel
CS	Carbon steel

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 σ-bond spinal column of overlapping *sp2* fusion orbitals. The residual out-of-plane Pz orbitals on the carbon atoms overlie with adjacent Pz orbitals to give π-bonds (Pi bonds). Also conjugated polymers have a skeleton of irregular single and double carbon-carbon bonds. The electrons that form the π-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 π-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, chromatesand 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 (TiO_2, SiO_2 and Al_2O_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 evaluatiing 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_2, PANI-SiO_2 and PANI-Al_2O_3) 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_2, PANI-SiO_2 and PANI-Al_2O_3).
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.

CHAPTER 2

LITERATURE REVIEW

2.1 Conductive Polymers

In (1985) MacDiarmid was the first one who suggested corrosion protection by inherently conductive polymers (ICPs). These polymers consist of conjugated chains containing π-electrons delocalized along the polymer backbone. In their natural form, ICPs are semiconductive materials that can be doped and converted into electrically conductive forms. The doping can be either oxidative or reductive; the oxidative doping is more common.

There are three states of ICPs: non-conducting (uncharged), oxidized (p-doped) where electrons are removed from the backbone and the reduced (n-doped) least common, where electrons are added to the backbone.

The doping processes are usually reversible, and typical conductivities can be switched between those of insulators (<10^{-10} S/cm) and those of metals (10^{5} S/cm) (Epstein, 1997). It can be synthesized both chemically and electrochemically. Electrochemically synthesis method has been observed that most ICPs produced by anodic oxidation enabling one to obtain a conducting film directly on a surface.

Polyaniline (PANI) is one of the most widely studied types of the ICPs for corrosion protection because it has several advantages over most conductive polymers. The advantages are: easy chemical and electrochemical polymerization, easy doping and de-doping by treatment with standard aqueous acid or base and high resistance to environmental degradation. PANI prepared by chemical polymerization: Aniline (monomer) is chemically polymerized using $(NH_4)_2S_2O_8$ APS in hydrogen chloride solution and electropolymerization (Figure 2.1).

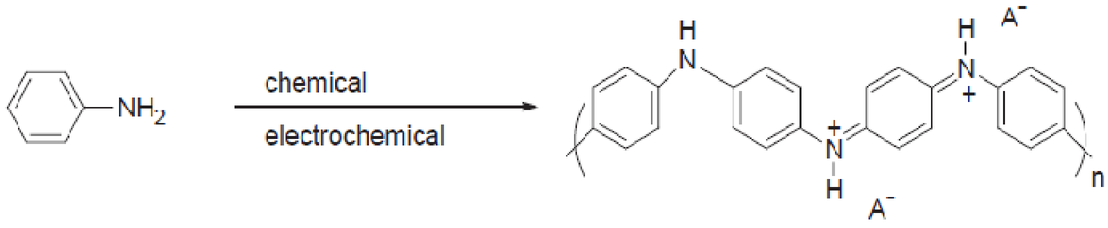


Figure 2.1 Synthesis PANI

PANI produced is an unusual ICP as it can exist in four different oxidation states. These states include; leucoemeraldine, pernigraniline, emeraldine base (EB) (intermediate form) and emeraldine salt (conductive form) Figure 2.2.

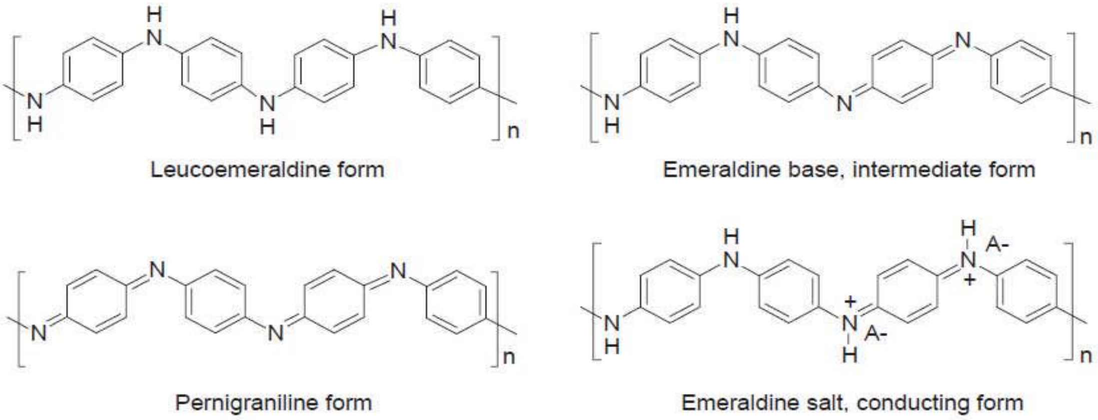


Figure 2.2 Oxidation states of PANI

PANI is normally prepared as the emeraldine salt (ES) from both chemical and electrochemical polymerization techniques, and by treatment with base, the EB form can be obtained. The doping process used to increase and decrease the electrical conductivity of PANI Fig.2.2 is by protonation (doping) and de-protonation (de-doping), respectively (Zarras *et al.*, 2003).

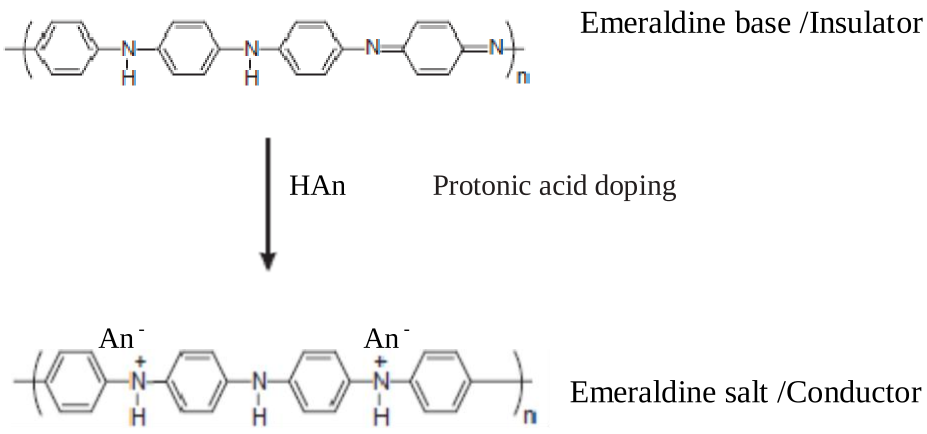


Figure 2.3 Protonic acid doping

The conducting form of PANI is emeraldine salt (ES), while the emeraldine base (EB) is non-conductive. Figure 2.3 shows the conventional formulas of ES and EB as well as the conversion between them by the doping–dedoping reactions. For example, positively charged nitrogen (N^+) was found in EB samples. Also, that EB does not have any oxygen-containing species but oxygen was found in EB.Among conducting polymers, polyaniline (PANI) is generally recognized to be one of the best candidate for an anti-corrosion coating, because of its ease of preparation, excellent environment stability, and interesting redox properties associated with the chain of Nitrogen (Kang *et al*., 1998).

It is suggested here to use the terms ‘‘undoped’’ and ‘‘doped’’ emeraldine instead of ‘‘emeraldine base’’ and ‘‘emeraldine salt’’ in the reversible doping–dedoping reaction scheme in Fig.2.3. The relation between the equilibrium concentrations may be represented by where [N^+] is used to designate the concentration of doped emeraldine, and [–N=] represents the concentration of undoped emeraldine (Jianguo Wang, 2002)

There exists a redox process between the conducting polymer and iron or metal.

Oxidation**:** reductant $\longrightarrow$ product + e^-

Loss of electron **and** oxidation number increase

Reduction**:** oxidant + e^- $\longrightarrow$ product Gain of electron **and** oxidation number decrease

2.2 Corrosion Theory:

Corrosion impacts our daily life naturally occurring chemical reactions that occur between a metal or a metal alloy and its environment. Corrosion costs to the US economy amounts to between 100 and 300 billion dollars annually. Infrastructure items that can be significantly damaged and eventually destroyed by corrosion include pipelines, bridges, automobiles, storage tanks, airplanes and ships. The most common environments for corrosion are in natural waters, atmospheric moisture, and rain man-made solutions.

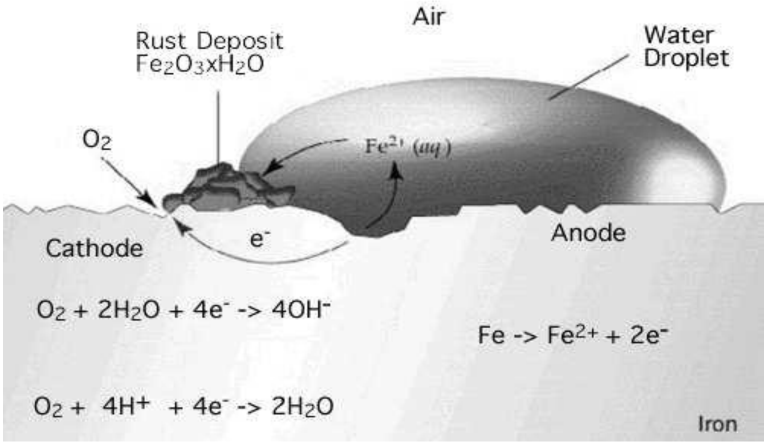


Figure 2.4 Corrosion mechanism

The corrosion resistance of steel is dominated by interactions between the constituents of the steel. The steel surface contains both anodic and cathodic sites. In the presence of a surface layer of water or other conducting solution an electric current passes between the anodes and cathodes. By convention the transmission of the current is by electrons, which are the electrical charges attached to atoms, and are generated at anodes. Their loss leaves the anodic areas deficient in electrons and iron goes into solution as ferrous ions.

$\mathbf{Fe} \longrightarrow \mathbf{Fe^{+2}} + \mathbf{2e^-}$

Iron Ferrous ions Electrons (anode reaction)

This reaction is the basis of the corrosion of iron. Electrons generated as shown above are consumed at the cathode area, and react there in various ways depending on the availability of oxygen. In normal atmospheric corrosion there is an ample supply of oxygen and the following reaction occurs.

$\mathbf{Fe} \longrightarrow \mathbf{Fe^{+2}} + \mathbf{2e^-}$ (anode reaction)

Iron Ferrous ions Electrons

$\mathbf{H_2O + 1/2\ O_2} + \mathbf{2e^-} \longrightarrow \mathbf{2OH}$ (cathode reaction)

Water Oxygen Electrons Hydroxyl Ions

The hydroxyl ions (OH^-) from the cathode combine with the ferrous ions (Fe^{+2}) from the Anode to form ferrous hydroxide, which is precipitated. This further reacts with oxygen and water to form hydrated ferric oxide, which is known as rust. As shown in Figure 2.4.

The rate of rust formation rapidly increases if the transfer of electrons from the anode to the cathode can be made easier; which happens if the conductivity of the water increases. This can occur due to the presence of dissolved salts, such as sea salts, on the surface or sulphur products from pollution fallout. In atmospheric corrosion it has been found that moisture is the controlling factor in the rate of rust formation and little rusting occurs unless the relative humidity is above 60-70%.In contact with acids corrosion increases because of direct attack on the metal, while under alkaline conditions the rusting of iron is inhibited.

Three methods may be used for rust prevention of Iron and steel:

a. Cathodic protection, that is, by employing another metal to be corroded or sacrificed instead of steel, such as the application of zinc rich paints, zinc being higher in the galvanic table, direct to the steel surface.

b. Applying a sufficiently thick layer of paint so that pores in the film do not form continuous capillary channels through the coating and water and oxygen are prevented from coming together to form the cathode reaction. This is the function of epoxy, vinyl and chlorinated rubber paints, which have high water impermeability.

c. An anti-corrosive paint applied direct to the steel surface and containing an inhibiting pigment will inhibit the occurrence of the anode reaction. This is the function of zinc or strontium chromate, barium metaborate and zinc phosphate pigments.. These coatings perform initially very well, but over time the barrier coating can fail due to prolonged exposure to the environment

2.3 Corrosion Protection by Polyaniline

Due to the excellent electrical and electronic properties and plastic nature of conducting polymers, they have been proposed for applications such as antistatic coating, corrosion inhibition coatings, electrochromic display, sensors, light-emitting diodes, capacitors, light weight batteries, and gas permeation membranes, etc. Among these applications, corrosion inhibition of metals has attracted much attention.

Both Polyaniline PANI and polypyrrole (PPY) have been shown to provide adequate protection against corrosion of aluminium alloys and steel (Kinlen et al., 2002; Su et al., 2000).

Polyaniline (PANI) is one of the most widely studied types of the ICPs for corrosion protection applications. There are three different configurations for the application of PANI coating have being reported: polyaniline coatings alone, polyaniline coatings as a primer with a conventional polymer topcoat and polyaniline blended with a conventional polymer coating.

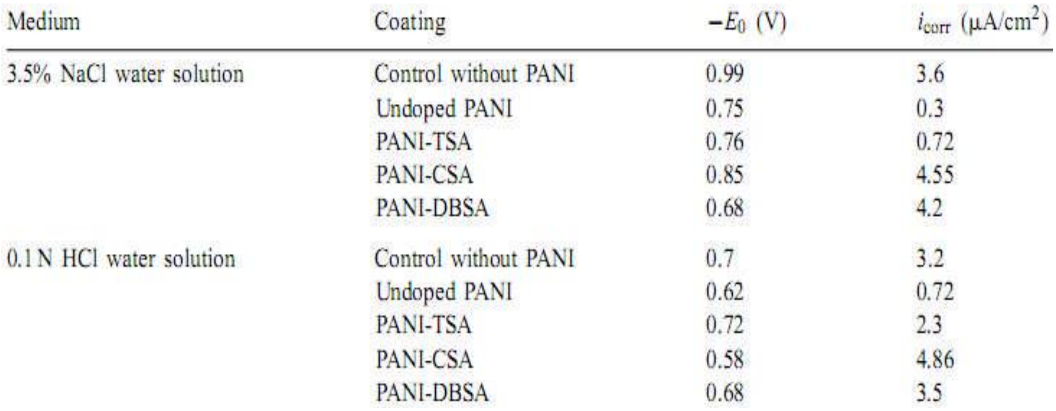
Comparisons of the performance of these three systems have shown that he primer/topcoat approach gives the most effective corrosion protection (Schauer *et al*., 1998) A number of studies have shown that he polyaniline primer/topcoat combination is better than topcoat-only also superior to primer/topcoat using primers conventional corrosion inhibitors like zinc. Also Schauer *et al*., (1998) showed three protective steps for conducting polymer participates in during corrosion protection such as:

a. Formation of passive layer by conducting form of PANI, PANI-HCl where the passive layer will be formed.
b. Spatial separation of cathodic and anodic partial reactions, short-lived as the HCl dopant is not expected to last long in air/water environment.
c. Improvement of barrier properties by dedoped PANI (PANI base) dedoped PANI containing paint will be left with improved barrier properties.

Chain conformations of doped polyaniline are influenced by several factors, such as solvents, chemical nature of a dopant, molar ratio of the dopant to PANI, and the polymer matrix in a blend. The conformation, on the other hand, strongly influences the distance of the delocalization of charge-carriers and in consequence conductivity of the sample (Jadwiga Laska, 2004).

That PANI coating can provide corrosion protection of aluminum alloy (Al 3003) both in neutral NaCl and in dilute HCl solutions. The degree of the corrosion protection of the alloy by the undoped PANI coating is higher than that of the doped PANI coatings and its maximal level is achieved in a neutral medium. Table 2.1 showed of the electrochemical monitoring of coats doped and undoped PANI on Al 3003 in 3.5% NaCl and 0.1N HCl solutions.

Table 2.1: Results of the electrochemical monitoring of coats for doped and undoped PANI



Medium	Coating	$-E_0$ (V)	i_{corr} ($\mu A/cm^2$)
3.5% NaCl water solution	Control without PANI	0.99	3.6
	Undoped PANI	0.75	0.3
	PANI-TSA	0.76	0.72
	PANI-CSA	0.85	4.55
	PANI-DBSA	0.68	4.2
0.1 N HCl water solution	Control without PANI	0.7	3.2
	Undoped PANI	0.62	0.72
	PANI-TSA	0.72	2.3
	PANI-CSA	0.58	4.86
	PANI-DBSA	0.68	3.5

The electrochemical behavior of the PANI coatings had some important differences between mild steel and the aluminum alloy. Based on the obtained corrosion currents, the thickness of the surface protective aluminum oxide layer was found to be the main causes possibly influence to inhibiting effect (Ogurtsov *et al.*, 2004).

According to Tüken *et al*. (2004), showed inherently conductive polymers (ICPs) such as Polypyrrole (PPy) and Polyaniline (PANI) were synthesized electrochemically on 1 µm thick Ni layer was electrodeposited on MS electrode then was investigated the corrosion protection of this polymer top coated Ni coating .

The Ni coated electrodes with conductive polymer (ICPs) top coat (MS/Ni/ICPs) and without top coat (MS/Ni) were achieved by using cyclic voltammetry technique.The corrosion performances investigated in 3.5% NaCl solution. The ICPs top coated Ni coatings exhibited much better protection efficiencies with respect to single Ni layer on MS, Polymers films exhibited important barrier property especially barrier property of Ni layer. It was also shown that PPy coating gave much better performance with respect to PANI, as a top coat on 1µm thick Ni layer on MS.

Local potentials and a coupling current between the bare area and the coated area can be measured with electrochemical impedance, whilst Raman spectroscopy yielded with an electrode having an artificial pinhole defect area. It was shown that the ICP is actually able to passivate the defect area of the substrate metal. The electrochemical kinetics leading to the passivity is essentially the same as those of the bare metal introduced into the same corrosion test solution. Local impedance evidence the passive state of the defect area, and the classical impedance measured with the overall potential and current does not allow the impedance of the defect area to be predicted (Dung Nguyen *et al*., 2004).

Electrochemical synthesis of PANI on mild steel was performed from sodium benzoate solution with no induction period. Epoxy coatings were successfully electrodeposited on mild steel modified by PAN (MS/PANI/EP) Figure 2.5.

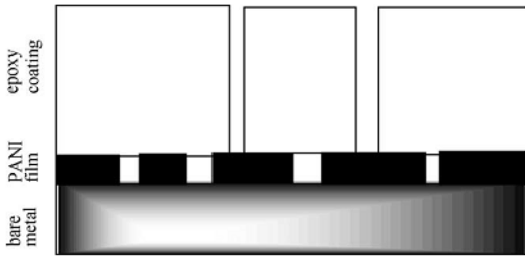


Figure 2.5 PANI/epoxy coated MS

Based on research conducted by Popović *et al.* (2005), that thin PANI Film had provided better corrosion protection if used primary coat under epoxy coating deposition. Enhance of the protective properties of PANI/epoxy coated mild steel is observed in higher values of the overall impedance, during cathodic deposition of epoxy coatings on PANI coated mild steel, de-doping of benzoate anions occurs rapidly, therefore during exposure to corrosion agent, the pores of the epoxy coating are not directly in contact with the bare metal, but with low conducting porous PANI film, PANI provides additional protection by its barrier effect.

Özyılmaz, A. T. *at el.* (2005), showed synthesis of polyaniline and applied by cyclic voltammetry to achieved on copper plate within neutral oxalate solution consequentially very adherent and homogeneous PANI film on copper (Cu/PANI) Corrosion protection by using PANI coating to protect copper was investigated, in chloride containing medium. It was found that the PANI coating could exhibit barrier behaviour against the attack of the metal by corrosive species.It was also shown that the presence of the PANI coating could enhance remarkably the protective behaviour of copper oxides. The PANI coating exhibited important catalytic effect on the formation of a protective oxide layer on the surface.

The second report produce by Özyılmaz, A. T. *at el.* (2005) regarding to Synthesize polyaniline (PANI) films electrochemically on Ni plated MS (MS/Ni/PANI) and unplated MS electrodes (MS/PANI). Electrochemical synthesis of polyaniline was carried out from 0.1 M monomer containing oxalic acid solution. The corrosion performance of these polymer films synthesized on different substrate was investigated in 3.5% NaCl. It was compared with the AC impedance diagrams and anodic polarization curves of PANI films obtained on nickel plated MS and bare MS.

The electrochemical process is:

$$Fe \longrightarrow Fe^{+2} + 2e$$

$$EM^{2+} + 2e^{-} \longrightarrow LE$$

$$1/2\ O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-}$$

These reactions must be caused by ion diffusion processes taking place through the pores of the coatings on the metal surface. Consequently, metal at the bottom pores of PANI coating is oxidized thereby yielding its oxides while polymer film is reduced at metal/polymer interface.These two events provided an increase in coating resistance. Mild steel which plated and unplated by Ni was successfully coated by polyaniline (MS and MS/Ni electrodes) which synthesized from 0.1 M aniline containing oxalic acid solution by cyclic voltammetry technique.

It was found out on MS electrode that the repassivation peak was not observable due to its porous oxides layer and nickel plating on the surface of mild steel and the passivation on MS/Ni was found to be possible in shorter time when compared with mild steel.

It was shown that MS/Ni/PANI exhibited much better barrier property for longer periods and the protective of nickel oxide layer increased with the enhance effect of polyaniline film in time

According to research reported by Özyılmaz, A. T. (2005), Polyaniline (PANI) synthesis by Electrochemical method and applied on 1µm thick Ni plated copper electrode (Cu/Ni) as a top coating (Cu/Ni/PANI) by cyclic voltammetry technique in 0.15M aniline containing sodium oxalate solution. The corrosion behavior of PANI top coated and uncoated electrodes nickel plating on copper electrode (Cu/Ni) was investigated using AC impedance spectroscopy (EIS).

Özyılmaz, A. T. (2006), showed almost same the previous report, Polyaniline (PANI) synthesis by Electrochemical method and applied on 1µm thick Ni plated copper electrode (Cu/Ni) as a top coating (Cu/Ni/PANI) by cyclic voltammetry technique in 0.1 M aniline containing *p*-toluenesulfonic acid (*p*-TSA) solution. While the medium in previous work was (0.15M aniline containing sodium oxalate scid solution).

Strongly and uniformly adherent PANI coatings on Cu/Ni and this top coating exhibited much better corrosion performance in chloride ions medium than single nickel plating. The accelerating effect of chloride ions contributed to reduce of polymer film at metal/polymer interface on formation of nickel oxides.AC impedance spectroscopy (EIS) results showed the impact of catalytic polymer film performed significant role on physical barrier property of nickel and its oxide layers and provided longer periods protection against attack of corrosive products.

On the other hand, Polyaniline (PANI) obtained by using cyclic voltammetry technique CV supported by electrolyte oxalic acid to coated Stainless steel (SS). The corrosion performances of these PANI coated electrodes (SS/PANI) were investigated by applying EIS electrochemical impedance spectroscopy technique and anodic polarization curves after (SS/PANI) immersion test in 0.05 M sulphuric acid H_2SO_4 and in 0.1 M hydrochloric acid HCl solutions with and anodic polarization curves. PANI/SS coating exhibited important barrier properties during 48 h of immersion times in chloride ions medium; however, this behavior decreased significantly due to deformation of polymer film. Corrosion protection properties of the SS/PANI passivated during electropolymerization due to adsorbed sulphate ions on metal surface as stable oxide layers and plugging of the pores. In this case, the sulphate ions limited the diffusion rate of ions toward metal surface and led to the decrease of the permeability of polymer coating. (Özyılmaz *et al.*, 2006).

Özyılmaz *et al*. (2006) also showed PANI were coated stainless 316L steel electrodes with applying two different scan rates in 0.1M aniline containing 0.3M oxalic acid solution. polyaniline films were obtained on (SS/PAN). However it was found that polyaniline film obtained at low scan rate had less porous structure with respect to high scan rate. SS/PANI-L exhibited important barrier effect against the corrosion for longer periods, but after 240h of immersion time this barrier effect decreased significantly for SS/PANI-H.

Zinc deposition on PANI Coating provided effective cathodic protection to MS for considerably long immersion period and lowered the permeability of polymer film also enhanced the cathodic protection efficiency by provide electrical conductivity between the substrate and zinc particles. Therefore, the zinc modified polymer coating exhibited effective barrier behavior against the attack of corrosive solution (Tuken *et al*., 2006).

Research observed by TunçTűken. (2006), it says that when the potential value is constant of −1.20V in 0.2M $ZnSO_4$ solution, Zinc particles have been electro deposited on Polypyrrole (PPy) and Polyaniline (PANI) coated copper samples successfully.The zinc particles lowered the permeability also the corrosion of zinc particles produced stable and voluminous products in immersion period in 3.5% NaCl solution which enhanced the barrier property of the coating. The cathodic protection produced effect against copper corrosion; the zinc particles provided cathodic protection to the substrate, where the polymer film played the role of conductance between zinc particles and copper.

Besides, Sathiyanarayanan *et al.* (2006e), used polydiphenylamine (PDPA) in vinyl coating for corrosion protection of steel in 3% NaCl solution. (PDPA) was prepared by chemical oxidative method of diphenylamine $(C_6H_5)_2NH$ by ammonium persulfate in HCl acid medium.The synthesized (PDPA) was blended with vinyl resin at 0–5% concentrations. 3% (PDPA) containing coating has been found is able to protect steel more effectively by evaluated the corrosion protection performance of the coating on steel by EIS of 80 days. During the oxidation process of iron to iron oxide, the PDPA (Ox) is reduced to PDPA (Re) form. The reduced form PDPA (Re) is re-oxidized to PDPA (Ox) form by dissolved oxygen reduction reaction.

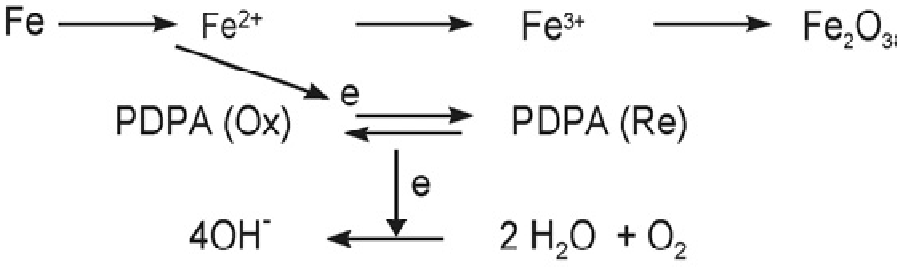


Figure 2.6 Mechanism of corrosion protection

by PDPA containing coating

The Polyaniline–amino tri methylene phosphoric acid (PANI–ATMP) was dispersed in epoxy resin, PANI–ATMP exhibits a crystalline structure similar to PANI and the UV–vis and IR of the PANI–ATMP are similar to those of PANI. The PANI–ATMP pigmented epoxy coating is found to offer corrosion resistance of steel exposed to saline environment evaluated by salt spray, open circuit potential measurements shifted to noble direction after the initial shift in the active direction in 3% NaCl and EIS. The increasing values of coating resistance with period of exposure indicate the high protective nature of the coating (Syed Azim *et al*., 2006).

There is an increasing interest on the use of (ICPs) to protect reactive metals against corrosion. At least four different configurations to apply ICPs coatings have been reported:

i. As a coatings alone.
ii. As a primer coating with a conventional topcoat.
iii. Blended with a conventional polymer coating.
iv. As an additive to modify a conventional organic coating.

Several mechanisms have been proposed to explain the protective role of electrochemically prepared coatings based on doped (ICPs). The first is based on the redox potentials of the (ICPs), which are more positive than those of metal substrates .However, it has been postulated that the protection of iron or steel by porous coatings of CP is not possible without a suitable passivation of the substrate surface before the film formation (Armelin *et al*.2007).

DeBerry (1985) has been reported that Polyaniline (PANI) and its derivatives are among the most frequently studied ICPs used for corrosion protection and has been of wide interest. In addition, that electroactive coating of the PANI could provide suitable protection against corrosion of stainless steels and iron sheets. Iron and different metals and alloys have been published in ICPs in different configurations were evaluated for corrosion protection and deposit an electroactive polymer on a metal surface in two methods chemically and electrochemically.

Solange de Souza (2007) have shown electrochemical behavior of a blend formed by (camphor sulphonate acid)-doped polyaniline PANI (CSA) used for iron, copper and silver. It was observed that the protection depends on the formation of a passive film between the polymeric coating and the metallic substrate.Raman spectroscopy clearly shows the loss of emeraldine character of PANI due to a redox reaction with the metal surface, and that the extent of the redox reaction depends on the metal. Metallic cations form a passivating complex with the dopant anion (camphorsulphonate), which improved the barrier property of different metals modified polyaniline coating system and lowered the permeability against the attack of corrosive solution, for long immersion period. In addition, the chemical interaction between (EB) and copper may also promote adhesion of the coating, making it more resistant to the cathodic delamination processes than pure (ER) coating (Chen *et al*., 2007).

Tansuğ et al. (2007) have made comparative epoxy-polyamine paint top coat on mild steel (MS/E) polyaniline (MS/PAni/E) and polypyrrole (MS/PPY/E) Figure 2.7 conductive polymers used as primary film on mild steel under epoxy-polyamine paint the top coat were investigated in 3.5% NaCl solution of pH 8.

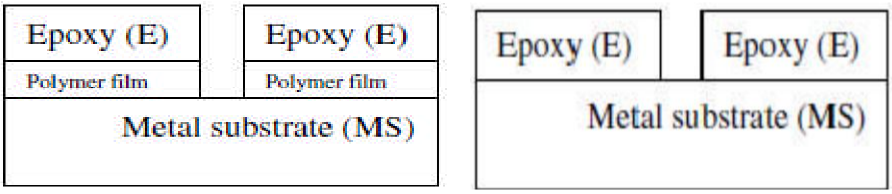


Figure 2.7 Representation MS\E and MS\polymer\E

Electrochemically synthesized very thin PPy and PANI films have been investigated as primary coatings on mild steel, under thick epoxy-polyamine applied by brush as top coat. Corrosion resistance to environment aggressive are decrease with PPy primary coating compared to a single epoxy coating in longer periods because, PPy has more film porous structure which allowed the progress of corrosive solution under the coating (by the water uptake process)Also, PPy film could not exhibit significant anodic protection behaviour for mild steel substrate. The primary PANI coating had lower permeability and better catalytic behaviour on passivation of steel, compared to PPy film.

In an alkaline environment, emeraldine salt is transformed into the deprotonated form of emeraldine base (Figure 1.2). The transition of the protonated form to the basic form of emeraldine takes place at pH 6–7. Emeraldine base has the same number of reduced (secondary amine) and oxidized (amine) groups. The investigation of anticorrosion efficiency of coatings with the PANI + Zn-dust combination found out that the PANI combination with a volume concentration (PVC) of 5% and Zn-dust achieves high anticorrosion efficiency (Kalendov´a *et al.*, 2008)

On the other hand, the investigation for corrosion protection of mild steel coupled with copper by full immersion test in 3.5% NaCl solution at 40°C coated by Polyaniline emeraldine base/epoxy resin (EB/ER) with 5–10% EB had long-term corrosion resistance. On steel–copper coupled plates due to the passivation affect of EB on the coupled metals surfaces on equal exposed surface areas of 3 cm×3 cm. However, immersion tests on coated steel–copper couple showed that emeraldine base/epoxy resin (EB/ER) coating offered 100 times more protection than epoxy resin (ER) coating against steel dissolution and coating delamination on copper, which was primarily attributed to the passive metal oxide films of Fe_2O_3/Fe_3O_4 and CuO/Cu_2O formed by EB blocking both the anodic and cathodic reactions.

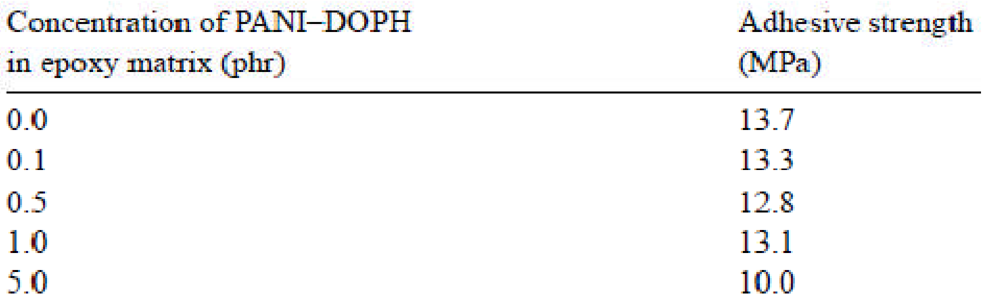
2.4 Polyaniline Doped in Corrosion Protection

Corrosion protection is enhanced when the PANI is used as a primer layer under a conventional barrier polymer as topcoat such as epoxy, Acrylic polyurethane…*et al*. However, the mechanisms of corrosion protection are complex and understanding these mechanisms is complicated by the many factors that influence the processes occurring. Comparison between primary coating of the polyaniline emeraldine base and polyaniline emeraldine salt doped affected the corrosion rate of coated steel with conventional coating. Quantitative analysis of iron-dissolution rates showed clearly differences between polyaniline doped with different ions when used with a polyurethane topcoat. However, the emeraldine base produced the lowest iron-dissolution rate over the period tested (Dominis *et al*., 2003).

The comparison with Cr (VI) post treatment based on impedance measurements shows anticorrosion performance of undoped PANI. This could be a clear result of the activity of undoped PANI in cathode effectively stabilizes coating system in an aggressive (1M NaCl, pH=4) environment (Kulszewicz-Bajer *et al.*, 1999).

Samui and Phadnis (2005) observed Polyaniline doped with dioctyl phosphate (PANI–DOPH) was incorporated as active pigment in various resins and coated mild steel panels (MS/ PANI–DOPH). FTIR spectra revealed the formation of an oxide layer on MS surface. Table 2.2 shows adhesion strength of the coating was found to decrease marginally after incorporating polyaniline.

Table 2.2 Adhesive strength of PANI–DOPH containing paint



Concentration of PANI–DOPH in epoxy matrix (phr)	Adhesive strength (MPa)
0.0	13.7
0.1	13.3
0.5	12.8
1.0	13.1
5.0	10.0

Impedance measurement and humidity cabinet exposure study indicated that 5 phr PANI–DOPH containing epoxy coating offers protective performance for longer period compared to other resins. FTIR spectra revealed the formation of an oxide layer on mild steel surface. There was no sign of corrosion on PANI–DOPH (5 phr)/epoxy coated MS panels compared to panels coated with different resins.

The mechanism of protection of iron by PANI containing coating is by the formation of passive film due to redox reaction of iron and PANI and also by the secondary reaction of formation of dopant–iron complex (Ngyen *et al.*, 2004).Hence the protection of iron takes place via the reduction of polyaniline emeraldine salt (PANI-ES) to polyaniline leucoemeraldine salt (PANI-LS) with the concomitant release of phosphate anions.

These released phosphate ions form iron–phosphate complex along with the passive film formed by PANI. The reduced PANI-LS can undergo re-oxidation to PANI-ES by the dissolved oxygen present in the medium. The evidence for re-oxidation of PANI-LS to PANI-ES by oxygen has been proved.

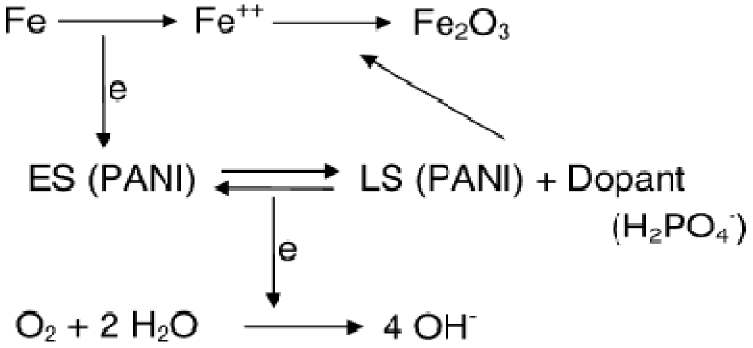


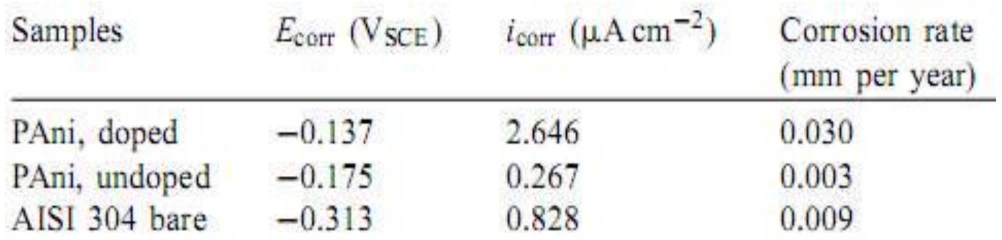
Figure 2.8 mechanism of protection of iron by PANI

The two forms of emeraldine PANI available; doped (conductive) and undoped (non-conductive) PANI in undoped emeraldine fewer studies are devoted to the corrosion protection properties in this form. Furthermore, there is difference of whether the conducting or non-conductive form of PAni exhibits the best corrosion protection properties (Fenelon *et al.*, 2005).

(Dominis *et al.*, 2003) found that emeraldine base coatings provided a better corrosion protection than the coatings based on a conductive PANI (EIS).the substance became in the passive region once coated using PANI emeraldine salt as primary coating. The type of PANI doping strongly influenced on PANI performance in terms of corrosion protection.

Stainless steel protect by PANI coating application from corrosion inhibitor in 3% NaCl solution, which is indicated by large shifts of the $E_{\mathbf{corr}}$ to more noble values compared to uncovered steel in both doped and undoped PANI forms are compared to that of the uncovered stainless steel surface as mention in **Table 2.3**

Table 2.3 Comparison for PANI doped, undoped and barer sample results



Samples	E_{corr} (V_{SCE})	i_{corr} ($\mu A\ cm^{-2}$)	Corrosion rate (mm per year)
PAni, doped	−0.137	2.646	0.030
PAni, undoped	−0.175	0.267	0.003
AISI 304 bare	−0.313	0.828	0.009

Corrosion current densities and corrosion rates of stainless steel uncoated and coated by PANI electrosynthesized in 0.6 M phosphate buffer (pH = 1.8).This inhibition effect depends on the oxidation state of the polymer as well as the characteristics of the passive layer formed on the metallic substrate (Moraes *et al.*,2003).

Corrosion protection of carbon steel by using undoped PANI Epoxy blend coating was studied. (EIS) measurements in 3.5% sodium chloride solution showed passivation characteristics of undoped PANI pigmented paint. The OCP was shifted to the noble region due to the passivation effect of PANI Epoxy pigment.EIS analysis confirmed the capacitive behavior of the PANI pigmented paint coating. It was found that after 300 days of immersing the resistance of coating, impedance was found about $4 \times 10^5 \Omega$ cm^2. Measuring of phase angle at 10 KHz frequency showed that there was a good agreement between coating resistance and phase angle. It seems that it could be a good criterion to evaluate this type of coatings (Akbarinezhad *et al*., 2008).

The most important form of PANI is a green protonated emeraldine that is conducting. Its conductivity is enabled by the presence of cation-radicals in its structure. Such emeraldine “salt” can be obtained by the polymerization of aniline in the presence of an appropriate acid (Abdiryim *et al*., 2005).

PANI-HCl containing paint films have barrier property appreciate in contributes for corrosion resistance. The paint system has shown appreciable corrosion resistance without any top barrier coat as well as Adhesion strength of paint on mild steel surface was found good during the exposure remains unaffected. Corrosion protection of mild steel by using PANI doped HCl containing paint without any top barrier coat the application of two different types of coatings, such as PANI primer and epoxy top coat, on same substrate. Mild steel panels did not undergo any corrosion after 1200 h exposure in Humidity cabinet, salt spray and underwater exposure thus, revealed that lower PANI-HCl doped containing paint protected Mild steel better compared to that containing higher PANI-HCl (Samui *et al*., 2003).

Kamaraj *et al*. (2009) has been studied the effect of benzoate doped polyaniline containing coating based on vinyl and acrylic resins on the iron protection. EIS studies have been made on the corrosion protection performance of vinyl coating on steel with 1% polyaniline in 0.1N HCl and 3%NaCl up to 100 days of exposure. It has been found that benzoate doped polyaniline containing coating has found to offer more protection in neutral media than that in acidic media due to passivating ability of benzoate ions. FTIR studies have shown that the polyaniline protects iron by formation of passive iron oxide film along with Fe–PANI complex.

Liu and Levon (1999) reported that An emeraldine base (EB) form of PANI was also found to be oxidized by the hardener. The oxidized form of polyaniline provides improved corrosion protection of metals than that of emeraldine base since the value of the standard electrode potential for the oxidized form of PANI is higher than that of EB. Additionally, the surfactant improves the wet adhesion property between the coating and the metal surface.

Armelin *et al*. (2009) reported that PAI-EB is very effective in inhibiting corrosion. Thus, panels coated with the unmodified epoxy paint are lees resistant against corrosion than those protected with epoxy + PANI-EB formulation. Besides, the epoxy + PANI-EB formulation provides more protection than the epoxy + PANI-ES and the epoxy + $Zn_3 (PO_4)_2$.These results incorporated with those obtained for other epoxy coatings containing conducting and electroactive polymers as anticorrosive additives indicate that the protection mechanism of PANI-EB is based on the ability of this polymer to store charge. As well as the highest protection was donated by epoxy + PANI-EB paint.

Ogurtsov *et al.* (2004) reported the degree of the corrosion protection of the Al 3003 alloy had been studied by using electrochemical impedance spectroscopy (EIS) and revealed that the pure undoped PANI coating is higher than that of the PANI doped with *p*-toluene-sulfonic, camphorsulfonic and dodecylbenzenesulfonic acids coatings and its maximal level is achieved in a neutral medium.

Electrical transport properties of phosphoric acid doped polyaniline are investigated by the measurements of low temperature conductivity and thermopower. Samples were prepared by chemical polymerization of aniline in aqueous solution of phosphoric acid at various ratios of acid to aniline (Z). The conductivity at room temperature increases from 3 S/cm to 40 S/cm (Yoon *et al.*, 1997).

Sathiyanarayana *et al.* (2008) described the corrosion protection performance of PANI doped phosphoric acid containing coating is comparable with that of chromate-containing coating. The PANI-phosphate polymer containing organic coatings are able to protect the aluminum alloy from corrosion due to the passivation ability of the polyaniline which is evidenced from the shift of open circuit potential in noble direction with time of exposure.

Kalendova *et al.* (2008) synthesized Polyaniline by phosphoric acid doped and applied as anticorrosion pigment in different volume concentration 3, 5, 10, 15, 20 and 24 vol. % containing coating. Kalendova *et al.* (2008) studied the effects of polyaniline volume concentration on the mechanical and corrosion resistance of the coatings, a number of paint films with increasing value of polyaniline volume concentration were prepared. Results of corrosion resistance revealed that the best corrosion resistivity was showed by organic coating containing 15%vol.concentration of Polyaniline pigment. This concentration facilitates the best anticorrosion effects of PANI in all the applied corrosion environments.

The corrosion performance of polyaniline doped with hydrochloric acid pigmented paint coating in 3% NaCl and 0.1N HCl solutions show that polyaniline pigmented coating on steel is highly corrosion resistant in both neutral and acidic media by electrochemical impedance spectroscopy (EIS) and the of corrosion protective property enhances as well (Sathiyanarayanan *et al.*, 2005).The mechanism of steel passivation by PANI coating is shown in Figure 2.9 Due to conducting nature of pigment, the oxygen reduction reaction takes place on the coating, while the oxidation of ferrous ions to iron oxides takes place on the exposed iron surface at pinhole areas and under the film in neutral media. However, in acid media the passivation of pin holes takes place by the cathodic complementary reaction. PANI conversion of LS in acid media, the coating is changed from conducting to non-conducting, cause by increased capacity behaviour of coating with immersion time.

$$\text{PANI (ES)} \longrightarrow \text{PANI (LS)}$$

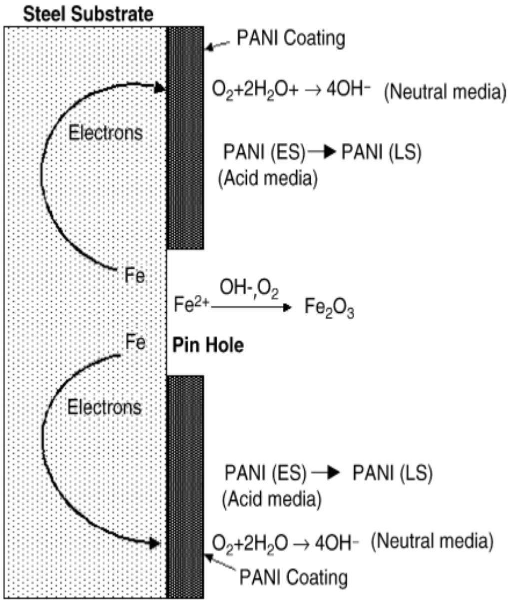


Figure 2.9 mechanism of iron passivation by PANI

Pigmented paint coating on steel.

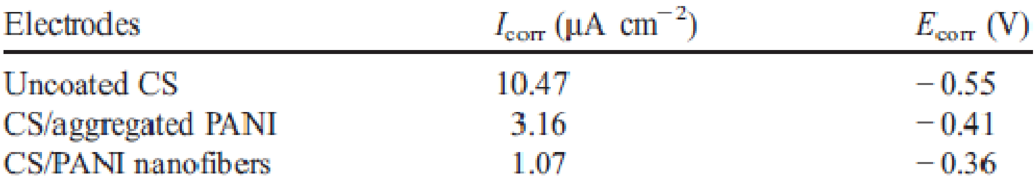
Sathiyanarayanan *et al.,* (2006a) reported that the corrosion performance of PANI prepared from equal amount HCl doped, aniline and oxidant agent. The PANI pigmented vinyl acrylic coating and evaluated by 0.1 N HCl, 3% NaCl and cement extract (pH 13.0). Carbon steel protected from corrosion in acid, neutral and alkaline media. The coating is found to passivate steel in neutral and alkaline media which is evidenced from the shift of open circuit potential value to noble value and from increase in paint film resistance for longer immersion period.

On the other hand, Sathiyanarayanan *et al.* (2006b) proposed corrosion protection using Phosphate doped polyaniline as pigment. PANI phosphate doped has been prepared by chemical oxidative method using equal amounts from aniline doped with phosphoric acid and ammonium persulphate APS as oxidant agent then characterized by FTIR and XRD methods to proved phosphoric acid doped PANI.The epoxy coating with the phosphate doped polyaniline pigment (CS/ epoxy paint+ PANI- phosphoric acid) is able to offer good protection to steel in 0.1N H_3PO_4 than in 0.1N HCl especially in 3% NaCl media.

In addition, Sathiyanarayanan *et al.* (2006c) reported Polyaniline doped by phosphoric acid blending with acrylic paint coated magnesium alloy ZM 21. With Same previous preparation method, PANI was prepared by chemical oxidative method of aniline with ammonium persulphate APS in phosphoric acid medium and the pigment has been characterized with FTIR and XRD as well .Corrosion protection performance for (ZM21/ acrylic paint+ PANI- phosphoric acid) evaluated and showed noble direction in open circuit potential values due to passivation ability of the Polyaniline and EIS reveal this coating was able to offer high protection to magnesium alloy in more than 75 days exposure to 0.5% NaCl sodium chloride solution.

Besides, Bin Yao *et al.* (2008) prepared polyaniline nanofiber by interfacial polymerization method. It is the first report for anti-corrosion properties of the polyaniline nanofiberss and aggregated PANI-coated on carbon steel samples exposed to 5% NaCl aqueous solution was evaluated **Table.2.4** by electrochemical corrosion measurements.

Table 2.4 results of uncoated CS and coated CS in 5% NaCl



Electrodes	I_{corr} (μA cm^{-2})	E_{corr} (V)
Uncoated CS	10.47	−0.55
CS/aggregated PANI	3.16	−0.41
CS/PANI nanofibers	1.07	−0.36

The results show that the carbon steel coated with PANI nanofibers has more excellent corrosion protection than that with aggregated PANI and the bands of the carbon steel coated PANI nanofibers are stronger than that of the carbon steel coated aggregated PANI. This is explane that PANI nanofibers have better passive effect to carbon steel. It could be explained that the PANI nanofibers have larger specific surface than the aggregated PANI, which easily adhered to carbon steel and form a fine structure for anti-corrosion.

The conclusion of this part of my literature by Amarnath *et al.* (2008) reported that the Polyaniline morphology of the nanostructures could be controlled by the playing dopnt selenious acid and aniline concentration. in situ-polymerization without use of any surfactant or template. Polyaniline with nanoflakes, nanorods and nanospheres was obtained when the aniline-selenious acid mole ratio is 1-0.03, 1-0.5 and 1-2, respectively.

The morphology transition was characterized using SEM studies and molecular structure of the polyaniline nanostructures was confirmed by XRD, FTIR and UV-vis spectroscopic techniques. Simply Gain three hybrid materials with various conductivity, crystallinity, nanosize and high surface area.

2.5 Corrosion Protection by Polyaniline Composite

Hybrid composite coatings containing zinc oxide (ZnO) and Polyaniline (PANI) as additives dispersions were prepared with poly (vinyl acetate) as the major matrix. The steel plates dip-coated with these formulations were tested for corrosion protection by immersion in saline water over long periods. The coatings containing both ZnO and PANI showed improved corrosion resistance as compared to the single component coating. The conducting PANI hybrid coating containing nanoparticulate ZnO in PVAc matrix shows remarkable improvement in corrosion protection of steel in saline water. The novelty of these coatings lies in generation of corrosion inhibition by three mechanisms operating simultaneously, viz. improvement of barrier properties, formation of p–n junctions preventing easy charge transport, and redox behavior of PANI when coating is threatened to be destroyed due to scratch or scribble. Apart from the prevention of corrosion, these coatings have good gloss and shiny surface (Patil and Radhakrishnan, 2006).

Sathiyanarayanan *et al.* (2007a) studied different ratios of aniline-Fe_2O_3 were taken to prepare polyaniline–Fe_2O_3 composites (PFC), i.e. 1:2, 1:1, 2:1. Using the prepared composites, primer paints with acrylic binder were prepared and coated on the steel samples.

(PFC) has been prepared by chemical oxidative method in the presence of aniline and Fe_2O_3 by ammonium persulphate oxidant in phosphoric acid medium and then characterized by FTIR, XRD and SEM. The corrosion resistant property of the coating containing 1:1 composite is found to be higher than that of Fe_2O_3 and other 1:2 and 2:1 polyaniline–Fe_2O_3 composites.

Most of the conventional coating contains iron oxide (Fe_2O_3) inorganic nanoparticle as one of the pigment with primer coatings to promote the ability for protection. Therefore, polyaniline–Fe_2O_3 composites containing coatings can exhibit better corrosion protection ability of iron. Earlier studies on polyaniline–Fe_2O_3 composites were mostly concerned with their conductivity and magnetic properties (Yang et al., 2003). Nanoclay also introduced into epoxy matrix epoxy/clay composite significantly improved physical and chemical properties such as toughness and stiffness were improved through the incorporation of nanoclay modified epoxy (Wang *et al*., 2006).

The corrosion protection effect of Polyaniline-clay nanocomposite (PCN) materials at low clay loading compared to conventional Polyaniline was demonstrated by a series of electrochemical measurements of corrosion potential, polarization resistance, and corrosion current on CRS in 5 wt % aqueous NaCl electrolyte. The coatings of PCN materials were found to offer good corrosion protection and showed a better anticorrosion performance than conventional Polyaniline coating. The as-synthesized PCN materials were characterized by FTIR, wide-angle powder X-ray diffraction and TEM. Permeability measurements, TGA, DSC, the incorporation of nanolayers of MMT clay in Polyaniline matrix resulted in a decrease in mechanical strength (in the form of free-standing films) and in thermal decomposition temperature (in the form of fine powders) based on the DMA and TGA studies. This might be attributed to the significantly decreased molecular weight of Polyanilines formed in the MMT clay.

Dispersed nanolayers of MMT clays in Polyaniline-clay nanocomposite materials led to a significant increase of crystalline temperature based on the DSC results (Yeh et al 2001).

Additionally, Olad and Rashidzadeh, (2008) studied the preparation PANI/MMT nanocomposites with hydrophilic and organophilic nanoclay particles was successfully performed by in situ polymerization method.

The electrical conductivity measurements showed that the PANI/MMT nanocomposite films are conductive with conductivities lower than pure polyaniline film in the case of PANI/Na-MMT nanocomposite and higher in the case of PANI/OMMT nanocomposite. The reversible electroactive behavior of PANI/MMT nanocomposites was confirmed by cyclic voltammetry technique. Results of the corrosion studies showed that the anticorrosive property of both hydrophilic and organophilic PANI/MMT nanocomposite coatings on iron samples is better than for pure polyaniline coating.

Kalendov´a *et al.* (2008) modified pigments by depositing PANI phosphate doped as surface layer on various anticorrosion pigment particles in paints. The original pigments and these pigments coated with PANI were tested and the PANI phosphate powder was tested as well. The concentration of pigment in paints was 15 vol. %. About 20 wt. % of PANI was present in the surface-modified pigments. The films based on pigment none modified such as iron oxides and silicate pigments exhibit similar results with PANI-coated pigments. The excellent results of anticorrosion efficiency were detected in the paint films with the content of graphite-based pigments. The PANI coating of the synthetic graphite and especially of the natural form of graphite contributed to the marked enhancement of the total anticorrosion efficiency of the paint film.

Besides, Kalendov´a *et al*. (2008) described the corrosion protection for four anticorrosion pigment improved after Coated with with PANI phosphate.Four pigments of various morphology(specularite, a-Fe_2O_3; goethite, a-FeO(OH); talc, ($Mg_3(OH)_2$-(Si_4O_{10}); and graphite, C) without and with polyaniline phosphate coating, had been the anticorrosion exam produced by epoxy coatings n iron samples. PANI into epoxy coatings reduces the hardness and improves the adhesion and ductility lamellar pigments have better overall anticorrosion performance.

All pigment improved the anticorrosion properties but Graphite coated with PANI Phosphate was the best one among four pigments after modification. Graphite got the higher conductivity after coating, which explains the best corrosion protection; promote the transfer of electrons in the redox reactions between iron and PANI or oxygen and PANI.

In marine atmosphere glass flake used to filled epoxy coatings are found to offer excellent protection and improved adhesion properties of the glass flake containing coating by incorporating In spite of ability of glass flake containing coatings for corrosion protection, there is some pinholes presence in the coating reduces the corrosion protection ability. Polyaniline containing coating is able to protect the pinhole defects in the coatings due to passivating ability of polyaniline. Hence a study Sathiyanarayanan *et al.* (2007b) has been made on the corrosion protection ability of steel using polyaniline–glass flake composite (PGFC) synthesized by chemical oxidation of aniline by ammonium persulphate in presence of glass flake containing coating with 10% loading of glass flake (GF) in epoxy binder. The corrosion protection ability of GF and PGFC containing coating on steel was assessed by using salt spray test and EIS test in 3% NaCl.

In both the tests, the resistance value of the (PGFC) containing coating has remained at $10^8\Omega10^9$ Ωcm^2 where as for the (GF) containing coating, the resistance values decreased to 10^5 Ωcm^2.The presence of polyaniline in the (PGFC) containing coating was able to enhance the corrosion protection by its passivation ability on metal surface.

Abu and Aoki (2005) founded the PANI–PS particles on the iron plate were useful to protect iron against corrosion. The films were stable at the iron surface at potential region where gas evolution occurred. The oxidized form of PANI–PS film showed better corrosion protection than its reduced form. The corrosion protection was demonstrated with the positive shift of the open circuit potential and the corrosion potential and by the decrease in the corrosion current.

The corrosion potential had the linear relation with the logarithm of the amount ratio of the oxidized PANI to the reduced PANI. Pure Polyaniline film on iron was obtained by removing PS latex by THF. This film showed anti-corrosion similar to the PANI–PS film and electrochemically synthesized PANI coated on iron. We can fabricate a large corrosion-protection film by painting the PANI–PS aqueous suspension on iron objects.

Ansari and Alikhani (2008) was found that PANI/Ny coatings can provide considerable protection, as well as a physical barrier against corrosive environments (e.g., NaCl, HCl) in which the metal are exposed. The corrosion rate for the polymer-coated steel was significantly lower than the bare steel (~10–15 times). Metal passivation (formation of a thin, compact, adherent, and passive layer of Fe_2O_3 at the interface) may be due to the redox catalytic effect of PANI.

2.5.1 Corrosion Protection by PANI-TiO_2 Composite

The anionic surfactant-coated TiO_2 suspension and doped PANI solution were combined to form homogeneous suspension and to cast free-standing nanocomposite films with the TiO_2 content up to 50 wt.%. Such processable PANI/TiO_2 nanocomposite has suitable conductivity (1^{-10} S/cm) when it is cast from the combined suspension, and it increases after thermal treatment at 80°C for 1 h. Such process able nanocomposite will be promising candidates for advanced materials to be used in the high-technology industries in the future, and work on the exploration of its applications is currently underway (Shi-Jian Su and Kuramoto, N. ,2000)

Organic coatings on metals are not perfect physical barriers against corrosion when they are in contact with aggressive species such as O_2 and H^+. These corrosive species can reach the substrate via coating defects. Electrically conductive polymers for example Polypyrrole (PPy) and Polyaniline (PANI) are capable of providing corrosion protection. This protection involves the use of chemical and electrochemical techniques such as chemical inhibitors, cathodic and anodic protections. Polypyrrole PPy/TiO_2 composite has been synthesized and applied as films on mild steel show good characteristics for the corrosion protection. Corrosion tests such as weight loss and salt spray tests show that TiO_2 improves the anticorrosion properties of PPy (Lenz *et al.*,2003).

Corrosion performance of epoxy coatings is promoted after modified by adding various ratios of nano-sized titanium powder. Corrosion performance of the modified epoxy was studied by electrochemical impedance spectroscopy (EIS) in 3.5% NaCl aqueous solution. Among the three percentages 5 wt. %, 10 wt. % or 20 wt. %, the coating with 10 wt. % nano-sized titanium powder possessed the best corrosion resistance among the coatings tested, which might have resulted from the lowest diffusion coefficient for the inward migration of aggressive media through the coating in the given system (Zhang *et al*., 2007).

Dc and Ac conductivities for different ratios of PANI–TiO_2 nanocomposite have been investigated. The change of PANI concentration did not influence significantly on the Dc conductivity. The Ac conductivity reveals a correlated barrier hopping type conduction process. It decreases considerably with increase of PANI content. The presence of TiO_2 nanoparticles does not change the charge transport mechanism of PANI but enhances the dielectric constant by about ten times that of pure PANI. The exact physical origins of the huge dielectric constant still remain unclear. (Dey *et al*., 2004).

According to Li *et al.* (2003) surface modification of TiO_2 nanoparticles by PANI has almost similar effect after composite. Results analysis suggests that the composite contains 10% conducting PANI by mass. WXRD and SEM micrograph show that the PANI has no effect on the crystallization performance and morphology of TiO_2 nanoparticles, but conductivity of PANI -TiO_2 composite has reached 2.9×10^{-2} S cm^{-1} at 20 °C. This result shows that molecular chain constitution of PANI is the most important carrier in the composite. FTIR and FT-Raman data have indicated that PANI and TiO_2 nanoparticles are simply not blended or mixed up.

A strong interaction exists at the interface of polyaniline macromolecule and nano-TiO_2 particles. The strong interactive force may be attributed to the tendency to form coordination compound between titanic and nitrogen atom in polyaniline macromolecule and the action of hydrogen bonding between nano-TiO_2 particles and PANI macromolecule. Combining the changes of the surface area, total pore volume and pore size distribution of nano-TiO_2 particles with that of PANI-TiO_2 composite particles, it can be concluded that polyaniline deposited on the surface of the nano-TiO_2 particles forms a core-shell structure. TEM clearly shows the PANI-TiO_2 core-shell composite for particles form (Li *et al*., 2004).

Conductivity of redoped PANI-TiO_2 prepared from *m*-cresol suspension is higher than that prepared from chloroform suspension because of well-extended conjugated chain of polyaniline. The second route enables the preparation of stable TiO_2 suspension, the solubilization of stiff PANI Chain, and the fabrication of free-standing nanocomposite films of PANI-TiO_2 by employing anionic surfactants, DBSA and PDBSA. Compared with the former method, the TiO_2 content of com posite film can be easily controlled by changing PANI-TiO_2 ratio. The nanocomposite film shows suitable conductivity (1–10 S/cm), and it increases after thermal treatment at 80°C for 1 h (Su and Kuramuto, 2000).

TiO_2-PANI nanocomposites have been prepared by means of *in situ* chemical oxidative polymerization. The results show that strong interactions (e.g. hydrogen bonds and coordinate bonds) exist at the interface between TiO_2 and PANI. The dispersion of TiO_2-PANI nanocomposites is better than that of TiO_2 particles. A reaction scheme for the deposition of PANI on the surface of TiO_2 nanoparticles and the chemical oxidative polymerization of ANI has been proposed.

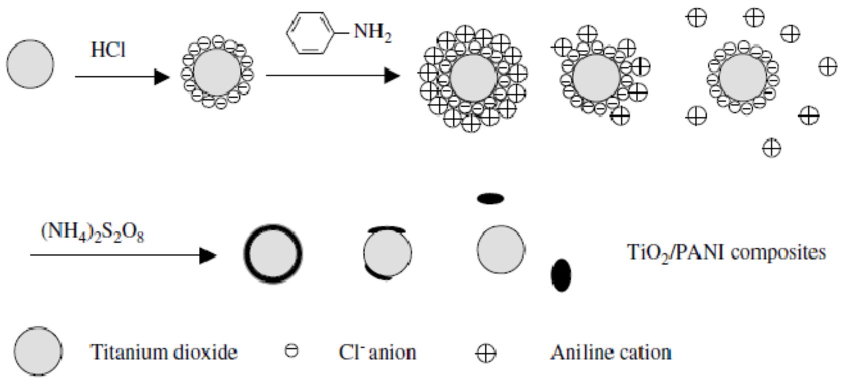


Figure 2.10 TiO_2 surface modified by PANI

The introduction of small amounts of PANI enhanced the dispersion of TiO_2 nanoparticles and the band gap energies of all PANI-TiO_2 nanocomposites were lower than that of neat TiO_2 nanoparticles, so the PANI-TiO_2 nanocomposites can be excited to produce more electron–hole pairs under sunlight, which could result in higher photocatalytic activities. nanoparticulate TiO_2 was modified by polyaniline (PANI) in order to enhance its photoactivity under UV light and sunlight illumination (Li *et al*., 2008).

Earlier studies on PANI–TiO_2 composites were mostly concerned with the synthesis and characterization and promoting properties new composite material such as conductivity, dispersion, thermal stability and so on. Sathiyanarayanan *et al*. (2007c) studied PANI–TiO_2 composite (PTC) by using in coating formulation since Polyaniline has been found to enhance the protective property of the coatings. (PTC) has been prepared by situ polymerization method of aniline by ammonium persulfate oxidant in the presence TiO_2. The XRD pattern shows that the Polyaniline has no effect on the crystalline behavior of TiO_2.

The SEM studies of PTC have shown that the TiO_2 particles are fully covered with Polyaniline. EIS studies of PTC containing coating in immersion tests in 3% NaCl and salt spray fog indicate that PTC containing coating is able to offer higher protection to steel from corrosion in comparison to conventional TiO_2 pigment containing coating due to passivation ability of Polyaniline.

Kinlen *et al*. (2002) have shown that polyaniline (PANI) containing organic coating on steel is able to passivate the pinholes and defects in the coating and passivation of metal surface through anodisation of metal by PANI and formation of an insoluble iron-dopant salt at the metal surface. TiO_2 is one of the main pigments which are usually used in the organic coatings.

Sathiyanarayanan *et al*. (2007d) presents the comparative corrosion protection performance of the coatings containing Polyaniline and polyaniline–TiO_2 composite (PTC) on steel in acrylic binder. The PANI and PTC were prepared by chemical oxidative method of aniline by ammonium persulfate method then characterized by FTIR, XRD and SEM. The FTIR spectra of PTC are similar to that of PANI.

XRD pattern of PTC indicates that the crystalinity of TiO_2 is not altered by PANI coating. The corrosion protection performance of the coatings containing PANI and PTC on steel was evaluated by immersion test in 3% NaCl for 60 days and salt fog test for 35 days have shown that the PTC containing coating has got higher corrosion resistant property than that of PANI containing coating. The higher corrosion protection ability of PTC containing coating may be due to the formation of uniform passive film on iron surface.

Besides, corrosion control of ferrous and non-ferrous metals such as magnesium ZM 21 alloy by acrylic paint containing Polyaniline and Polyaniline–TiO_2 composite (PTC) also was chemically prepared and characterized by FTIR,XRD and SEM. reported that the evaluation of coating containing PANI and (PTC) by electrochemical impedance spectroscopy (EIS) after exposure to salt spray test for a period of 250 h.The corrosion protection ability of PTC containing coating is found to be more than that of PANI containing coating due to the uniform distribution of PANI which can protect the metal surface more uniformly (Sathiyanarayanan *et al.*, 2007e).

Table 2.5 shows Preparation of nano-TiO_2–PANI hybrid coating formulations in different ratios (0, 0.1, 0.2, 0.3 and 0.5 g of TiO_2 nanoparticles)PANI–nano-TiO_2 using 10% with polyvinyl butyral (PVB) as the final coatings and investigating their suitability for anticorrosive coatings on stainless steel (SS).

Table 2.5 Synthesis of PANI–nano-TiO_2 composites with different composition and Composition of coatings made from 10% of above PANI–nano-TiO_2.

Sample	**Anilinewt (g)**	**TiO_2 wt(g)**	**Composite yield(g)**	**TiO_2%in product**	**PANI (wt%)**	**TiO_2 (wt%)**	**PVB (wt%)**
PANI	1.00	0.0	0.63	0	0.1	0.0	100
PANI 10	1.00	0.1	0.76	13	8.7	1.3	90
PANI 20	1.00	0.2	0.87	23	7.7	2.3	90
PANI 30	1.00	0.3	1.05	28.5	7.15	2.85	90
PANI 50	1.00	0.5	1.195	41.8	5.82	4.18	90

More than 100 times improvement in the corrosion resistance especially for polyaniline prepared with 4.18 wt% nano-TiO_2. Addition of nano-TiO_2 has been reinforcing corrosion inhibition by three mechanisms operating at the same time. Improvement of barrier properties, redox behaviour of PANI and formation of p–n junctions preventing easy charge transport when coating is threatened to be destroyed due to scratch. These coatings have good bright and shiny surface, which is not easily obtained in conventional coating, prepared with commercial micron size particle additives (Radhakrishnan *et al.*, 2009).

Electrochemical synthesize of Anodic alumina films with polyaniline and TiO_2 nanoparticles in oxalic acid electrolyte containing dissolved aniline and dispersed TiO_2 nanoparticles on AA3105 aluminium alloy. Corrosion protection for this coating was studied by electrochemical impedance spectroscopy (EIS) and salt spray test (SST).

Aluminium specimens coated with alumina aluminapolyaniline-TiO_2 (APT) film did not reveal corrosion products after 1000 h of exposure, while the specimens' coatings without TiO_2 nanoparticles detected the corrosion below 168 h for exposure time in (SST).Besides that, coatings containing TiO_2 nanoparticles present higher corrosion resistance values in (EIS) analysis. Coatings containing TiO_2 nanoparticles provide improved protection is attributed to the TiO_2 thin film layer formed on the outer part of the coating that acts as a blocking barrier layer for the anodic porous aluminium oxide film (Zubillaga *et al.*, 2008).

2.5.2 PANI-SiO_2 Composite

The addition of nano-$TiO_2$and nano-SiO_2 to epoxy resin significantly improved the corrosion resistance indicated by results of electrochemical impedance spectrum (EIS) and salt spray test. The dispersion and effects of nano-TiO_2 and nano-SiO_2 particles on the performance of epoxy resin on 2024-T3 aluminum alloy have been investigated by Shi *at el.* (2008). As well as the hardness of epoxy resin it was improved by the incorporation of 1 wt. % nano-TiO_2 particles or nano-SiO_2.

Kamada *et al.* (2005) studied the incorporation of oxide nanoparticles into alumina films, with anodic oxidation of the aluminium and electrophoretic deposition of nanoparticles proceeding in a single step. Alumina films containing SiO_2 nanoparticles showed an increase in the capacitance and improved corrosion protection of the substrate. The incorporation of SiO_2 nanoparticles into the nano sized pores of anodic alumina films was also examined, with the surface charge and size of the nanoparticles considered to be significant in enabling nanoparticles to migrate to the substrate during anodizing with subsequent incorporation into the anodic film.

In situ hybrids (Epoxy resin -TiO_2) and blend hybrids (Epoxy resin /SiO_2) were prepared by different procedures. It was estimated from SAXS measurements that these hybrids had different microstructures. In the *in situ* hybrids, TiO_2 domains were formed on both ends of the epoxy resin, and exerted strong interactions between the TiO_2 and the epoxy matrices.

On the other hand, in the blend hybrids, nano-particles of silica were randomly dispersed in the epoxy matrices, and the interactions between the silica particles and the epoxy matrices were weak. These microstructures reflect on the mechanical properties of the epoxy hybrids. The storage modulus, E', of the *in situ* hybrids increased markedly with TiO_2 content above the Tg, while the intensity of the tan δ peak decreased. In contrast, E' of the blend hybrids increased slightly with SiO_2 content, and the tan δ peak was sharp and large, although its intensity was unchanged (Yano *et al*., 2005)

Silicon dioxide was used to improve the toughness of epoxy resin as described by Zhang et al. (2006) the Impact resistance of the neat epoxy or epoxy/SiO_2 cured system was determined at room temperature by a falling dart impact tester. The distribution of SiO_2 and the fracture morphology of composites were examined using scanning electron microscopy (SEM) after impact testing. The thermal properties of epoxy/SiO_2 composites were studied by thermo-gravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis.The results showed that the incorporation of nano-SiO_2 effectively improved the toughness of cycloaliphatic epoxy resin as well as its thermal stability.

Further, Yao *et al*. (2008) reported fracture characterizations of SiO_2/epoxy nanocomposite are experimentally studied by means of SEM and FE-SEM. The microscopic fracture characterizations and crack propagation behavior are analyzed by means of SEM and FE-SEM. The influences of nanoparticle SiO_2 content on fracture behaviors of nanocomposites are analyzed. The results showed that the nanocomposite with 3% wt nanoparticle has higher fracture toughness and larger deformation resisting capability than other nanocomposites. The research results will be useful for structure design and fracture properties evaluation of nanocomposites.

Li *et al.* (2007) modified the epoxy resin with nano-SiO_2 and standard SiO_2 particles with diameter 30–40 nm and 3 μm, respectively. Thermogravimetric analysis, impact strength and bulk resistivity tests showed that initial decomposition temperature T_d, impact strength and bulk resistivity of epoxy resin-based composite increased and then decreased after nano-SiO_2 content reached 4 wt.%. Modification role of nano-SiO_2 in epoxy resin-based composite was more effective than that of standard SiO_2 due to large specific surface area and active groups on surfaces of nano-SiO_2 particles.SEM analysis showed that toughness of nano-SiO_2/epoxy resin-based composite and standard SiO_2/epoxy resin-based composite also increased and then decreased after nano-SiO_2 and standard SiO_2 content reached 4 wt.%.

On the other hand, new hybrid material produced from composite conductive polymer such as polyaniline with silicon dioxide SiO_2. polyaniline/nano-SiO_2 composite was obtained by surface modification of nano-SiO_2 particles using 15% polyaniline by mass, and was characterized via (FTIR), UV–vis , X-ray, (TGA), (TEM), and conductivity. The conductivity of polyaniline/nano-SiO_2 composite containing 15% polyaniline is 0.32 S cm^{-1} at 25°C. Apparently, polyaniline molecules are the most important carriers in polyaniline/nano-SiO_2 composite.

Although its conductivity is lower than pure polyaniline prepared at the same condition (1.3 S cm^{-1}).Besides, TG Analysis shows that the temperature of thermal decomposition of polyaniline/nano-SiO_2 composite is about 435 8C, which is lower than that of pure polyaniline. The drop in temperature may be associated with the effect of nano-SiO_2 particles upon polyaniline macromolecule. (Li *et al.*, 2005).

Dutta and De (2007) they proposed In the Polyaniline/SiO_2 synthesis process, monomer aniline is first adsorbed on the surface of SiO_2 particle. Upon addition of oxidant, polymerization takes place on the surface of each particle. Thus SiO_2 nanoparticle acts as the core for the growth of polymer chain.The effective surface area increases with the increase of SiO_2 concentration and as a result of it, the amount of aniline associated with each SiO_2 particle is diminished. The incorporation of silica reduces the conjugation length of PANI as evidence from the enhancement of π–π* gap estimated from absorption spectra. The conductivity of polymers primarily depends on the conjugation length. The insulating behavior of silica and the reduction of chain length lead to decrease in conductivity with increase of particle content. Conducting PANI is the charge carrier medium in the nanocomposite. Charge transport occurs between the localized states similar to disordered semiconductors.

Also Dutta and De (2006) mentioned The change in conductivity with different compositions of PPY and understanding of the conduction process is an important issue in nanocomposites because the Conductivity of SiO_2 is very low compared to PPY. the electrical conduction in polypyrrole–silica nanocomposite mainly come from conducting polypyrrole. The change in energetic position in π–π* transition of polypyrrole indicates a strong interaction with silica.

Herein, Neoh *et al.* (1999) used electroactive polymers such as Polyaniline PAN-SiO_2 and Polypyrrole PPY-SiO_2 nanocomposites for the uptake of gold and palladium from $AuCl_3$ and $PdCl_2$ in acid solutions respectively was investigated. The change in the physicochemical properties of the nanocomposites with metal uptake were of particular interest.High rates of uptake can only be achieved with the electroactive polymers reduced to their lowest oxidation state. The results showed that the electroactive polymer–SiO_2 nanocomposites represent a potentially useful material not only for recovery of precious metal but also for catalytic applications.

Withal Li *et al* .(2008) detected water-dispersible conducting by PANI/nano-SiO_2 composite with a conductivity of 0.071 S cm^{-1}at 25°C.The composite was prepared by presence of amorphous nano-SiO_2 particles during the oxidative polymerization of aniline. The method employed was very simple and inexpensive in comparison with methods applied by other researchers; Samples (0.001 g) were dispersed in 10 mL de-ionized water under ultrasonic action. It is hopeful to be used in commercial applications of conducting polyaniline/nano-SiO_2 composite as environmental protection fillers for antistatic and anticorrosion coatings.

2.5.3 PANI-Al_2O_3 Composite

One of the most popular methods for corrosion protection of metallic materials by Polymeric coating metal surfaces (Bierwagen.,1996) The corrosion protection mechanism can be employ as physicochemical barrier or an electrochemical one (inhibition or cathodic protection), or both of them and (Herrasti et al.,2001).According to fillers used in the coatings.

Among these, the inhibitive metal oxides are considered as effective corrosion inhibitors, such as chromate or Molybdate. With consideration, the healthy risk require to finding out another candidate wich has similar efficacy as well as health and environmental friendly. As we mention earlier, PANI is one of the promising candidates and has been extensively studied in both the doped and the undoped states.

The low prices of the materials are one of the important issues; it is one of concerning point in industrial field. Therefore, improving of the protective performance for organic coating by PANI composite alumina (Al_2O_3) particles is one of our aims. Additionally, the adhesion strength of organic coating is one of the factors which are influence upon protection. Zhai et al. (2007) proved that an increase in adhesion is achieved by alumina (Al_2O_3) nano particles addition in an epoxy adhesive employed into an epoxy adhesive to improve the adhesion strength with steel and measured the adhesion strength by adhesion test. The results showed that the adhesion strength has noticeable increased by addition of nano-Al_2O_3 into the epoxy adhesive compared with that of pure epoxy adhesive. The highest adhesion strength was obtained with 2wt% nano-Al_2O_3 in epoxy adhesive, being almost four times higher than that of the unmodified (Zhai et al., 2006)

Zhao and Li (2008) successfully used Spherical alumina (Al_2O_3) nano particles were incorporated into epoxy resin and investigate the effect of water absorption on the mechanical and dielectric properties of the Al_2O_3/epoxy nano composites.Tensile tests revealed that the incorporation of the Al_2O_3 nano particles into the epoxy can improve the stiffness of the matrix.The stiffness improved at the rubbery state of the matrix clearly showed by DMA results. Besides, the dielectric constant of the epoxy resin increased with Al_2O_3 nano particles incorporated due to the increase in the total interfacial area.

The mechanical properties of the Al_2O_3/epoxy nano composites decrease clearly in water absorption, because of the damage of water on the epoxy resin. However, the ductility can be improved by the water absorption process. Moreover, greatly increasing after water absorption treatment in dielectric constant and dielectric loss of the Al_2O_3/epoxy nano composites Micrometer-sized aluminum particles are grinded together with white spirit and used as pigments inhibition.

The pigment particles are flake shaped with a broad size distribution. The aluminum pigment often in the form of a paste packed with a volatile organic compound or dried as a powder (Karlsson et al., 2006).

Water borne paints and inks are being developed as a response to the increasing demands from different authorities and organizations to replace solvent borne coatings with more environment friendly alternatives (Niemann, j., 1992).Aluminum-flake pigmented in organic coatings having different flake orientations depends on preparation by various spray conditions. The preparation of aluminum pigments as flak shape in particular orientations of individual flakes were the best particle shape for best pigment properties which is determined inhibition properties and other enhancement of coatings properties and the determination from optical reflectance measurements(Sung *et al.*,2001).

Polypyrrole is one of the important conductive polymers. Polypyrrole composite with Al_2O_3 PPY-Al_2O_3 revealed interesting for morphological feature in SEM and TEM analyses. In terms of thermal stability which enhanced after PPY-Al_2O_3 composite clearly showed by TG analyses and Dc conductivities of PPY-Al_2O_3 composite were in the order of $(63\pm3$ to $33\pm5) \times 10^{-2}$ S/cm. this composite present new class material containing inorganic core which is coated uniformly by conductive polymer Polypyrrole. These new hybrid materials promising for new application in numerous fields that presence increasing their own properties, which are not possible to get it from each individual component (Ray., 2002).

Besides, (Teoh *et al.*, 2007) have prepared Polyaniline composite with Al_2O_3 nano fibers which is clearly demonstrated in TEM and FESEM. The XRD diffract grams indicated that the composite has the emeraldine structure.

The DSC and the FTIR studies showed that the composite was formed from interaction between the polymer and the Al_2O_3. The conductivity of the composite decreased with an increase in the Al_2O_3 content incorporated.

In terms of corrosion protection coatings, Tallman *et al.*, (2008) had been Report of making nano composite of alumina nano particles modified by Polypyrrole for the purpose of corrosion protection of Aluminum alloy. Modified nano particles were used as coating filler in relatively small concentration (less or equal to 2%).Coating was designated to perform as an active barrier to electrolyte diffusion. Properties of the coating were examined by adhesion test, X-ray, SEM, TEM, FTIR and Dielectric behavior of the coatings indicative to its swelling was studied by the electrochemical impedance spectroscopy (EIS).Coatings demonstrated protective behavior when exposed to corrosive environment.

On the other hand, Polypyrrole was synthesized in the presence of aluminum flake to produce polypyrrole/aluminum flake hybrids. The resulting flakes were incorporated into a standard epoxy coating at relatively high pigment volume concentrations with the end goal of producing a conducting film capable of providing corrosion inhibition to an aluminum alloy. The nature of various pigment volume concentrations of both as received pigment and pigment modified during a polypyrrole synthesis was probed utilizing (EIS). The results show that electrochemical impedance is sensitive to the amount of conductive polypyrrole/aluminum flake that was in the coating as described by Qi *et al.* (2008).

According to Zhang (2006) resulting core–shell structured alumina–polyaniline (Al_2O_3-PANI) particles. The polymerization of ANI occurred preferentially on the surfaces of the particles.

Morphology examination showed that with decreasing of the weight ratio of Al_2O_3/ANI in the reactants, the thickness of the PANI layer increased **(**Fig.2.13) with decreasing of the weight ratio of Al_2O_3/ANI in the reactants and changed from an even surface morphology to a particulate morphology.

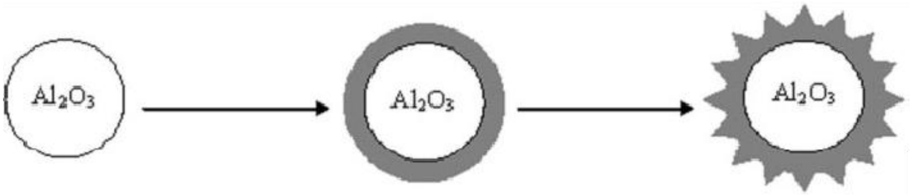


Figure 2.11 Formation of Al_2O_3-PANI particles with decreasing of the weight ratio of Al_2O_3 in the reactants.

UV–vis and (FTIR) spectra indicated that there is no chemical interaction between the PANI layer and the Al_2O_3 surfaces. The PANI layer adhered well to the particles and can be used as anticorrosive fillers for polymer coatings. The corrosion protection performance of the epoxy coating was greatly enhanced on carbon steel in 3.0 wt % aqueous NaCl solutions by use of the Al_2O_3-EB particles as fillers, and the cost was lowered by using of the alumina particles, which is of great importance in practical applications.

2.6 Conclusion

Intrinsically conductive polymers ICPs used for enhance anticorrosion properties with conventional coating especially (PANI) recognized to be the best candidate for enhancing anticorrosion paint due to its anticorrosion ability, easy for preparation, excellent environment stability, interesting redox properties associated with the chain of nitrogen ,environmentally friendly and safe to use comparing with other toxic pigment such as chromate.Scientific research going forward for promoting the coatings against corrosion through applied PANI as primary coating under the conventional coating or blend it with coating in several ratios looking for best one. PANI doped with different acid in various ratios, looking forward to the best anticorrosion performance. As well as, PANI synthesized using several methods for the purpose of obtaining applicable nanoform coupling with distinctive characteristics. Otherwise, PANI composite with various materials in terms of anticorrosion pigments applications especially metal oxides such as (TiO_2, Fe_2O_3 and ZnO). Likewise the compositions of PANI with effective anticorrosion pigments, such as ; MMT, glass flack and amino tri methylene phosphoric (ATMP).all this pigments used to composite with to PANI conductive polymer to improve the pigments performance for corrosion inhibition.

According to literature, phosphoric acid has been the best polyaniline doping terms of corrosion protection. Further, the ratio of doped is dissimilar and the percentage of morality is value. Furthermore, in situ polymerization method, aniline-doped ratios dominate PANI nanoforms. Hence first objective of this study focused on best polyaniline nanoform in corrosion protection. Secondly, whilst the SiO_2, Al_2O_3 and TiO_2 used as organic coating pigments and enhancing anticorrosion properties. Moreover, (SiO_2, Al_2O_3 and TiO_2) promoted after modified with PANI (PANI-SiO_2, PANI-Al_2O_3 and PANI-TiO_2).Hence, this three composites had been selected to used as a pigments in organic coating may well be the promising composites pigments in corrosion protection applications.

CHAPTER 3

METHODOLOGY

3.1 Materials

The starting materials used in synthesis PANI in different ratios and three PANI composites are shown in Table 3.1

Table 3.1: The starting materials used for preparation PANI and PANI composites

Materials	Usage	Brand
Aniline	Monomer	Mallinckrodt U.S.A
Phosphoric Acid (H_3PO_4)	Dopant	MERCK Germany
Titanium dioxide (TiO_2)	Composite core	MERCK Germany
Silicone dioxide (SiO_2)	Composite core	Emory Germany
Aluminum oxide (Al_2O_3)	Composite core	Fisher scientific U.K.
Ammonium persulphate $(NH_4)_2S_2O_8$	Oxidant agent	QRëC Germany
Acrylic paint	Paint coating	Nippon paint Malaysia
Sodium chloride (NaCl)	Immersion test	MERCK Germany
Carbon steel plates	Corrosion Surface /Test	Kross instrument

3.2 Instruments

The laboratory instruments which were used in pigments equipping and paint preparation included:

1. 1000 ml three neck round bottom flask with stirrer for PANI polymerization process
2. 500 ml beaker
3. Filtration paper for filtering pigments after polymerization by de-ions water
4. Oven for dry pigments after filtering 24 hours 55C°
5. Mixer (IKA digital motor stirrer) to blending pigments with acrylic coating
6. Grit paper (600) used for purifying surface of carbon steel specimens before paint it.
7. Graduating cylinder for measuring solutions
8. Pipette used for withdrawing solutions out for bottles.
9. Optical microscope (Leica DM IRM)
10. Cyclic corrosion cabinet model. SF/450/CCT
11. Digital camera (canon 10 MP) for visually observe corrosion on sample surfaces after end of exposed period.

3.3 Synthesis of PANI and PANI Composite

First, four separate solution of 200 ml of 1M of aniline was dissolved in distillated water by magnetic stirring. After completely dissolved and during the stirring Ortho-Phosphoric acid added by dropper with four different molarities (2M, 1M, 0.5M and 0.1M) after half an hour constant stirring Table3.2, Pre-cooled 200 ml of 1 M solution of ammonium persulphate was added drop wise to the pre-cooled aniline-acid mixture for about 2 hours with continue constant stirring. The reaction was conducted at 5±1 °C. The stirring continued further for another 3 hours for ensuring complete polymerization.

Secondly, in case of preparing polyaniline composite with inorganic particles, 1M of Al_2O_3, SiO_2 and TiO_2 powders were added in to 200 ml of 1M of aniline was dissolved in distillated water and doped with 1M Ortho-Phosphoric acid to be equivalent ratios for to (monomer-acid) for ensure each monomer has been doped. After added the powders in the solution, the mixture was stirred for 30 minutes to separate the powder from aggregation of inorganic particles and gives more chance and time to deposite aniline monomer on particles surface. Pre-cooled 200 ml of 1 M solution of ammonium persulfate was added drop wise to the cooled aniline-acid mixture for about 2 hours with continue constant stirring. The reaction was conducted at 5±1 °C. The stirring continued further for another 3 hours for ensuring complete polymerization. A dark green colored polyaniline (supposed to be the conducting form) was collected on a Büchner funnel, and the cake was washed several times with de-ionized water to remove excess acid content until the filtrate became almost colorless. The polymer was dried in oven at about 55 °C for 24 hours. Pigments were ground using mortar for lessening pigments aggregations before blending with acrylic paint.

Table 3.2: Starting materials and molarities for seven pigments

Sample	Monomer	Dopant	Composite
PANI	1 M Aniline	0.1M H_3Po_4	Non
PANI	1 M Aniline	0.5M H_3Po_4	Non
PANI	1 M Aniline	1M H_3Po_4	Non
PANI	1M aniline	2M H_3Po_4	Non
PANI	1M aniline	1M H_3Po_4	1M Al_2O_3
PANI	1M aniline	1M H_3Po_4	1M SiO_2
PANI	1M aniline	1M H_3Po_4	1M TiO_2

3.4 Preparation Pigments and Samples

The coatings were prepared by using solvent based vinyl acrylate wall sealer based industrial coating. The pigments were grinded finely and mixed with paint using lab attritor for 30 minutes. The loading of pigment included PANI, and PANI composite were kept 10% by volume with 20 % of Acrylic paint. The main pigments were four PANI doped with different acid molarities and PANI composite with three inorganic particles. The prepared coatings were kept in air tight jar.

To perform standard ASTM G31 of carbon steel samples will be prepared. Samples were polished with emery papers (600grit), clean, degreased with acetone ultrasonically and stored in dry atmosphere, dried and weighed with an accuracy of ± 1 mg. The panels were dip coated first for 15 sec in acrylic paint and with an interval of 15 mints for first dryness, and then samples will re-dipped again 15 sec in the same paint as second layer then leaved to dry 24 hour in room temperature. The prepared samples were ready for corrosion testing.

3.5 Pigments Characterization

3.5.1 Fourier Transforms Infrared Spectroscopy (FTIR-Perkin Elmer Spectrum)

PANI and PANI-composite will be characterized by Fourier transform infrared spectroscopy (FTIR) (FTIR-PerkinElmer spectrum) analysis technique that provides informationon structural features of the chains molecule via an infrared absorption spectrum. FTIR is very useful for identifying chemical, either organic or inorganic. It can be utilized to quantity some compounds of the unknown mixture. In various forms of solid, liquid and gas. In this research PANI, PANI-TiO_2, PANI-SiO_2 and PANI-Al_2O_3 is characterizedusing Perkin Elmer spectrum 2000 explorer FTIR spectroscopy. Measurement ranges from 370-4000 cm^{-1} with a 4 cm^{-1} resolution, 0.475-1/s scan speed and 16 scans. Small quantities (3-6 mg) of each sample dispersed in 5-10% with dry potassium bromide (KBr). Each mixture have been mixed thorough mortar and then pressed at pressure of 6 bars within two minutes to form moisture-free KBr thin disk. The thin discs have been placed in sample cap of diffuse reflectance accessory.

Molecules that has been exposed to infrared rays absorbs infrared energy at frequency which is characteristics of that molecule. Based on the IR-spectra, qualitative differences in the distribution of functional groups on the blend have been observed and evaluated. The transmission and reflectance are schematically represented in Figure 3.1.

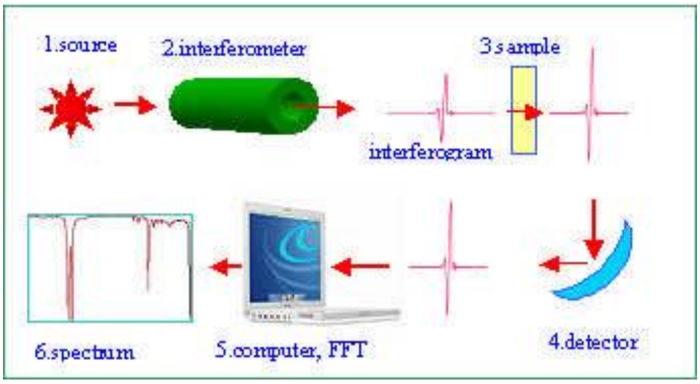


Figure 3.1 Schematic representations of the FTIR radiation path and their components.

3.5.2 X-Ray Diffract Meter (XRD) Siemens Model (Diffraktometer D5000)

X-ray diffraction is a versatile useful in terms of knowledge of crystalline phases of solid materials and powders form as well. In addition to structure properties detection such as, phase composition and modification. The method uses a beam of X-rays to bombard a sample from several angles. The X-rays are diffracted from successive planes formed by the crystal lattice of the material, according to Bragg's law: $n\lambda = 2d\sin\theta$ with n is an integer, λ is the X-ray wavelength, d is the distance between crystal lattice planes and θ is diffraction angle (Figure 3.2). Through angles evaluation and the diffraction pattern, can shows and determine sample the characteristic properly.

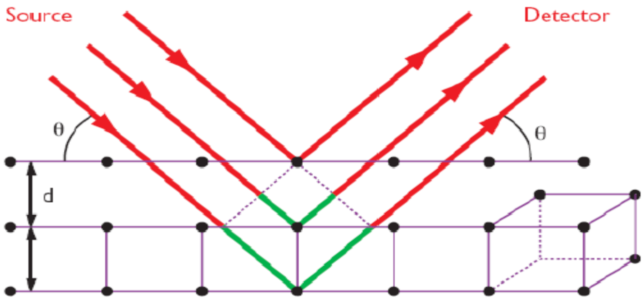


Figure 3.2 Diffraction of X-rays in a crystalline material.

3.6 Morphology

3.6.1 (SEM) Scanning Electron microscopy JEOL (JSM-6390LV) Model.

Upon completion of polymerization especially PANI composite with inorganic pigments, materials have to test using SEM instrument for morphology observation. The SEM confirm is PANI nanoparticles shielded the inorganic particles (SiO_2,$TiO_2$and Al_2O_3) or at least the PANI nanoparticles are deposited on the inorganic particles surface. This material can be new hybrid material which is having new promising properties. (SEM) JEOL (JSM-6390LV) model with magnifies an image at X 1,00 and X 2,500 by sending a beam of light through the object. The condenser lens focus the light on the sample and the objective lens magnifies the beams, which contain the image to the projector lens so that image was viewed by the observer. The SEM scanning electron microscope is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

3.6.2 (FE-SEM) Field Emission scanning Electron microscopy (FESEM-JEOL JSM6701F)

In terms of used polyaniline in corrosion protection which was prepared by for various ratio of monomer with dopant. FESEM has high magnification in case of monitor the nano particles size. Therefore we used the FE-SEM to observe formality changing in polyaniline structure.

3.7 Pigments Conductivity (Digital Multimeter CP7676 Actron)

The conductivity of seven pigments has been obtained by measuring resistance using digital Multimeter by taken average of ten deferent points for each pigment. The powders were pressed into a pellet of 1.29 cm diameter and 0.19 cm thickness under pressure. The pigments resistance was measured at room temperature. Samples were dried in vacuum before making into pellets. The conductivity collected through measuring the pellets resistance and applies equation 3.1 below:

$$\text{Conductivity (S/cm)} = \frac{1}{\text{Resistance}(\Omega)} \text{ / diameter (cm)} \qquad (3.1)$$

3.8 Dispersion Stability Test

Dispersion stability test for PANI prepared with four different ratios of monomer-doped (Aniline-Phosphoric acid) for the purpose of study PANI nanostructure preferable in term of dispersion stability. Samples were dispersing using ultrasonication in ethanol medium. The dispersion stability test is act at six increasable periods, start once stopping the stirring action until 24 hours. This test is valuable to select the best PANI nanostructure which is distributed appropriately in coating for corrosion protection application.

3.9 Corrosion Studies

3.9.1 Full Immersion Tests

The anticorrosion properties of the coatings were evaluated by total immersion test according to ASTM G 31. All the panels were placed in special designed apparatus mentioned in ASTM G 31 as shown in Figure 20 for 60 days at room temperature. After completing the period, the samples were taken out and cleaned according to ASTM G 1 and weighed again. The procedure of cleaning the samples consists of two steps. In the first step coatings were removed by using acetone as a solvent and in second step corrosion product were removed by taking 500 mL of hydrochloric acid (HCl, specific gravity 1.19) to which 3.5 g of hexamethylene tetramine was added. Distilled water was added to make it 1000 ml. The samples were dipped for 10 min at room temperature and cleaned with brush. The weight loss method was adopted to evaluate the corrosion rate. All the calculations are mentioned in Table 3.2 the equation 3.2 for weight loss method is as below:

$$\text{Corrosion Rate } \frac{K \times W}{A \times T \times D} \tag{3.2}$$

K = a constant,

T = time of exposure,

A = area in cm^2,

W = mass loss,

D = density

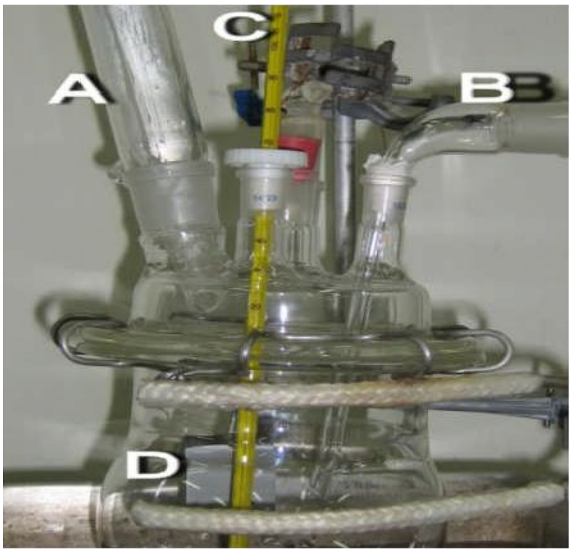


Figure 3.3: Typical Resin flask for immersion test, *A* = Condenser, *B* = Air inlet, *C* = Thermometer D = Sample hung

3.9.2 Salt Spray Chamber

Second corrosion evaluation method was followed according to standard ASTM B117 using salt spray chamber. The carbon steel specimens were polished with emery papers (600grit), clean, degreased with acetone ultrasonically and stored in dry atmosphere, dried and by acrylic paint containing our seven pigments used applied brush. Samples were leaved 24 hours then making equal scratch in the middle of each sample .the samples placed in cyclic corrosion cabinet under salt spray fog 35days. After finished exposed period the samples will be taken out and then monitor the rust by digital camera.

Figure 3.4 salt spray fog chambers

3.10 Adhesion and Thickness Tests

Adhesion test we had used ASTM D3359 methods for test the adhesion of coatings modified with seven pigments. After finish exposed periods in salt spray chamber, coating adhesion being tested using tape pull-up test to the cross line scratches area. As well as the thickness measurement it was under ASTM D 1186 stander by using electronic instrument (MiniTest 600B).

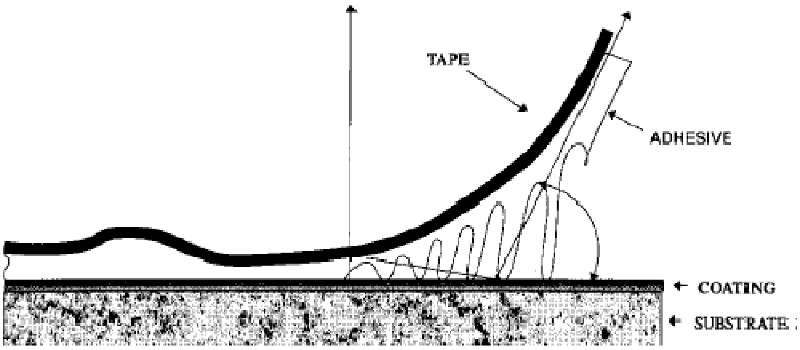
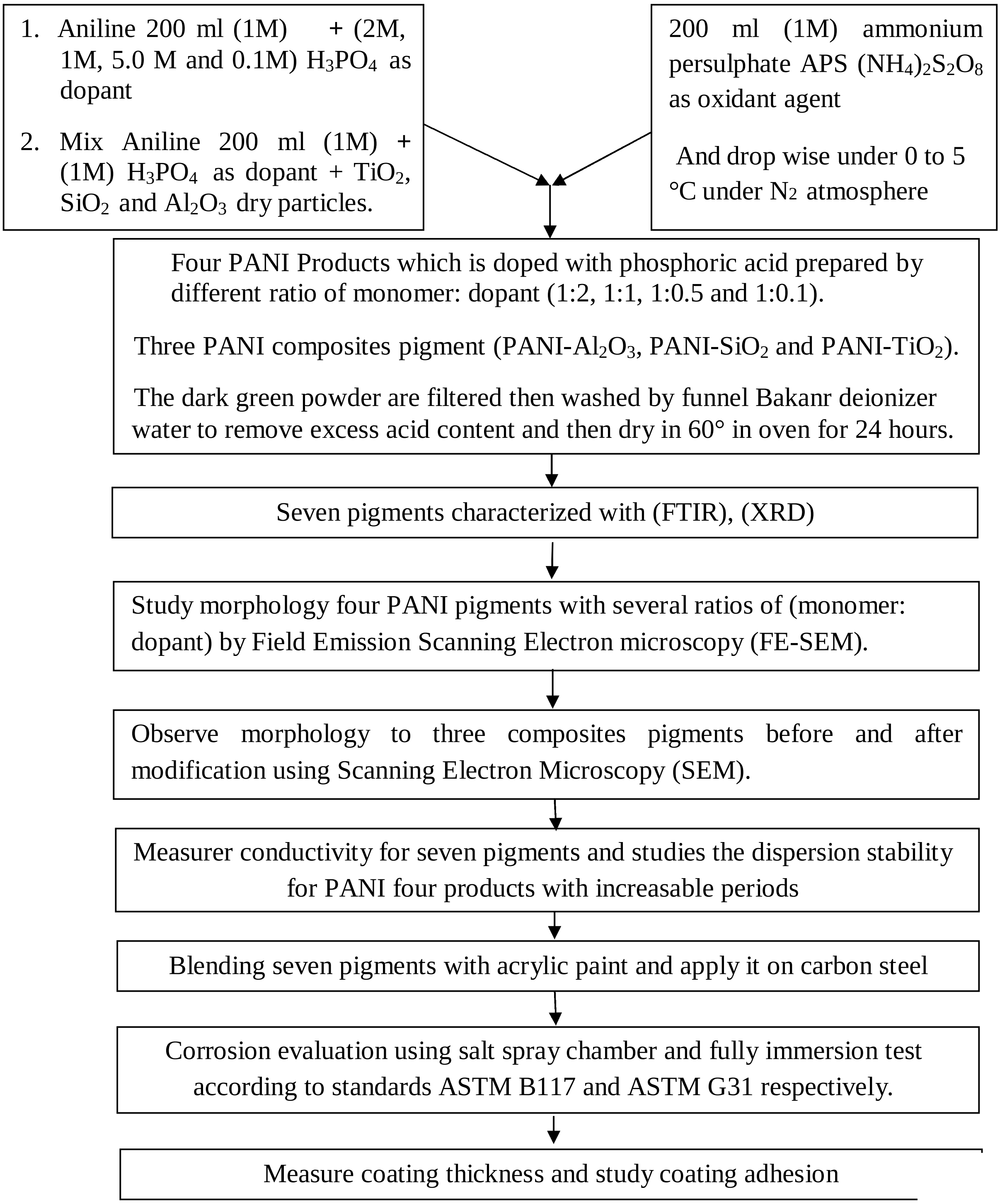


Figure 3.5 Tape pull-up test

3.11 Procedure Diagram

Figure 3.6 shows the procedure for preparation and characterization of PANI composite and corrosion evaluation.



1. Aniline 200 ml (1M) + (2M, 1M, 5.0 M and 0.1M) H_3PO_4 as dopant
2. Mix Aniline 200 ml (1M) + (1M) H_3PO_4 as dopant + TiO_2, SiO_2 and Al_2O_3 dry particles.

200 ml (1M) ammonium persulphate APS $(NH_4)_2S_2O_8$ as oxidant agent

And drop wise under 0 to 5 °C under N_2 atmosphere

Four PANI Products which is doped with phosphoric acid prepared by different ratio of monomer: dopant (1:2, 1:1, 1:0.5 and 1:0.1).

Three PANI composites pigment (PANI-Al_2O_3, PANI-SiO_2 and PANI-TiO_2).

The dark green powder are filtered then washed by funnel Bakanr deionizer water to remove excess acid content and then dry in 60° in oven for 24 hours.

Seven pigments characterized with (FTIR), (XRD)

Study morphology four PANI pigments with several ratios of (monomer: dopant) by Field Emission Scanning Electron microscopy (FE-SEM).

Observe morphology to three composites pigments before and after modification using Scanning Electron Microscopy (SEM).

Measurer conductivity for seven pigments and studies the dispersion stability for PANI four products with increasable periods

Blending seven pigments with acrylic paint and apply it on carbon steel

Corrosion evaluation using salt spray chamber and fully immersion test according to standards ASTM B117 and ASTM G31 respectively.

Measure coating thickness and study coating adhesion

Figure 3.6: Work procedure

CHAPTER 4

RESULTS AND DISCUSSION

4.1 FTIR Spectra Analysis:

PANI with four different molarities of phosphoric acid doped with aniline-monomer has three different nanostructures (nanospheres, nanoroad and nanofiber) but the FTIR spectra (a) of all the PANI nanostructures characterization almost similar (Palaniappan and Amarnath, 2005). The presence of two bands near to 1500 and 1600cm^{-1} are assigned to the non symmetric C_6 ring stretching modes. The higher frequency vibration at around 1600 cm^{-1} is for the quinoid rings, while the lower frequency modes around 1500 cm^{-1} describing the presence of benzenoid ring units. The frequency vibration at around 1300 cm^{-1} is for the C-N stretch of Q-B-Q and the frequency around 1250 cm^{-1} refer to C-N stretch of benzenoid ring. The peak around 1000 cm^{-1} has been assigned to $H_2PO_4^-$ peaks (Pu et *al*., 2005). Also the H_3PO_4 dopant anions present on PANI are dihydrogen phosphate anions, $H_2PO_4^{\,-}$ (Stejskal *et al*., 2004).

Figure 4.1 shows IR spectra for PANI and PANI composites with three different inorganic oxides:

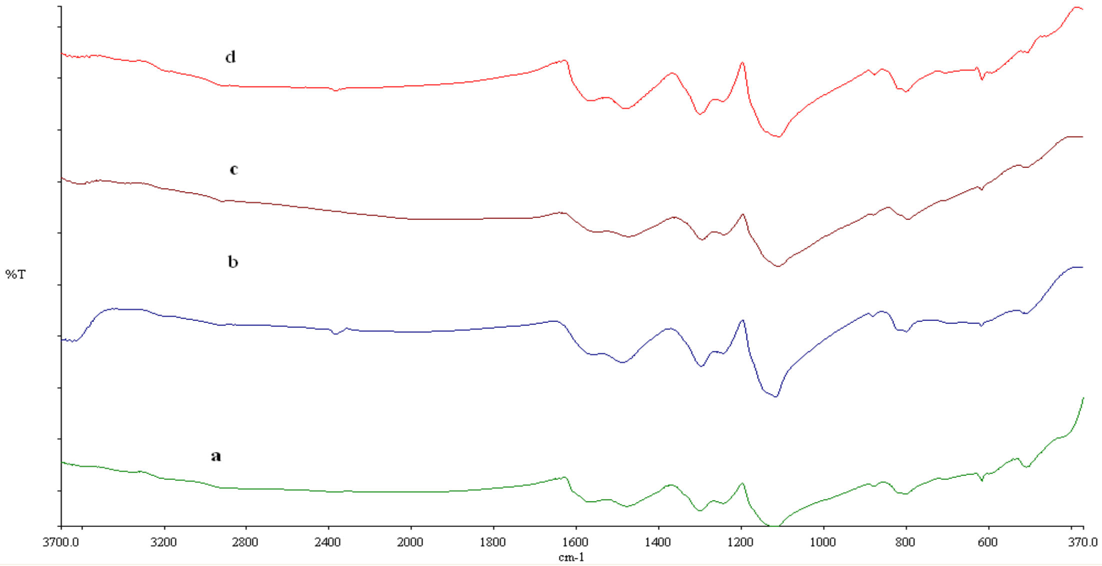


Figure 4.1 FTIR spectra a: PANI, b: PANI-TiO_2 composite, c: PANI-SiO_2 composite and d: PANI-Al_2O_3composite

In additional, the peaks around 1250 cm^{-1} and 800 cm^{-1} peaks are assigned to vibrations associated with the C-N stretching vibration of aromatic amine. The aromatic C-H bending in the plane (1107 cm^{-1}) and out of plane (800 cm^{-1}) for a 1, 4 disubstituted aromatic rings (Tarachiwin *et al*.2002) indicates a linear structure.

In terms of polyaniline composite, the spectrum shows that composites contain all the main characteristics of bands of polyaniline. But these peaks when compared to that of pure polyaniline (Li *et al*.2004) are found to be shifted slightly due to strong attraction of Al_2O_3 and TiO_2 particles with polyaniline. Similar observation has been reported by (Lee *et al* .2005). In the case of TiO_2, strong absorption around 670 cm^{-1} due to Ti–O stretching (Xu *et al*.2005).

Table 4.1 IR spectral data of pure PANI and PANI composites

ASSIGNMENT	PURE PANI PEAK (cm^{-1})	COMPOSITES PANI PEAK		REFERENCES
C=N stretch of quinoid ring (N=Q=N)	1567	1567		(Tang *et al.*,1988) (Sathiyanarayanan *et al.*,2006c) (Sathiyanarayanan *et al.*,2007e)
C=C benzenoid ring stretch (N-B-N)	1478	1478		(Cao *et al.*,1986) (Sathiyanarayanan *et al.*, 2006b)
C-N stretch of Q-B-Q	1296	1296		(Sathiyanarayanan *et al.*, 2007e)
C-N stretch of benzenoid ring	1244	1244		(Sathiyanarayanan *et al.*, 2007d) (Kang *et al.*,1998)
out-of-plane C-H bending	800	800		(Tarachiwin *et al.*2002)
ASSIGNMENT	**PURE PANI PEAK (cm^{-1})**	**Inorganic peaks and bond (cm^{-1})**	**C-H Peaks after composites(cm^{-1})**	**REFERENCES**
in-plane C-H bending	1117	650 (Al –O)	1108.5	(Teoh *et al.*,2007) (Lee *et al* .,2005)
in-plane C-H bending	1117	670 (Ti-O)	1106.5	(Xu *et al.*,2005) (Li *et al.*,2004)
in-plane C-H bending	1117	1083 (Si-O)	1109	(Li *et al.*, 2005).

The strong band at 1000–1125 cm^{-1} due to in plane C–H bending of PANI in the composites shifted to a slightly lower frequency appears stronger in comparison with the PANI, indicating significant interactions between the polymer and Al_2O_3 (Teoh *et al* .2007).

Besides, PANI-SiO_2 and pure Polyaniline are difficult to assign the absorption peaks of the composite because the SiO_2 particles and doped polyaniline absorb at similar wave numbers. By comparing the two, there are some polyaniline peaks which are shifted due to interactions with SiO_2 particles (Li *et al*. 2005). Similarly, the peak at 1106 cm^{-1}, formed upon protonation, also shifts to 1109 cm^{-1}.

4.2 X-Ray Diffraction

XRD pattern of three inorganic oxides TiO_2, SiO_2, Al_2O_3 and compositions with PANI suggests nearly similar between the two the XRD pattern of three inorganic particles before and after composite with Polyaniline. Further, the broad diffraction peak of PANI at $2\theta = 25^{\circ}$ is absent in the PANI-TiO_2 ,SiO_2 and Al_2O_3 which indicates that the presence of TiO_2, SiO_2 and Al_2O_3 in the polymerization system strongly affects the crystalline behavior of PANI form and the interaction of PANI with TiO_2 ,SiO_2 and Al_2O_3 narrowing the crystallization of PANI. This indicates that PANI deposited on the surface of particles has no effect on the crystalline structure of TiO_2, SiO_2 and Al_2O_3. Besides, these results indicate that PANI is amorphous in the PANI–Fe_2O_3 composite since the molecular chain of the adsorbed PANI is confined and the degree of crystallinity is decreased (Sathiyanarayanan *et al*.2007). It also confirms that the polyaniline deposited on the surface of particles has no effect on the crystallization behavior of TiO_2 and Al_2O_3 particles (Lee *et al*.,2005) and Similar observation on the XRD pattern is being reported for polyaniline–SiO_2 (Li *et al*. 2005).

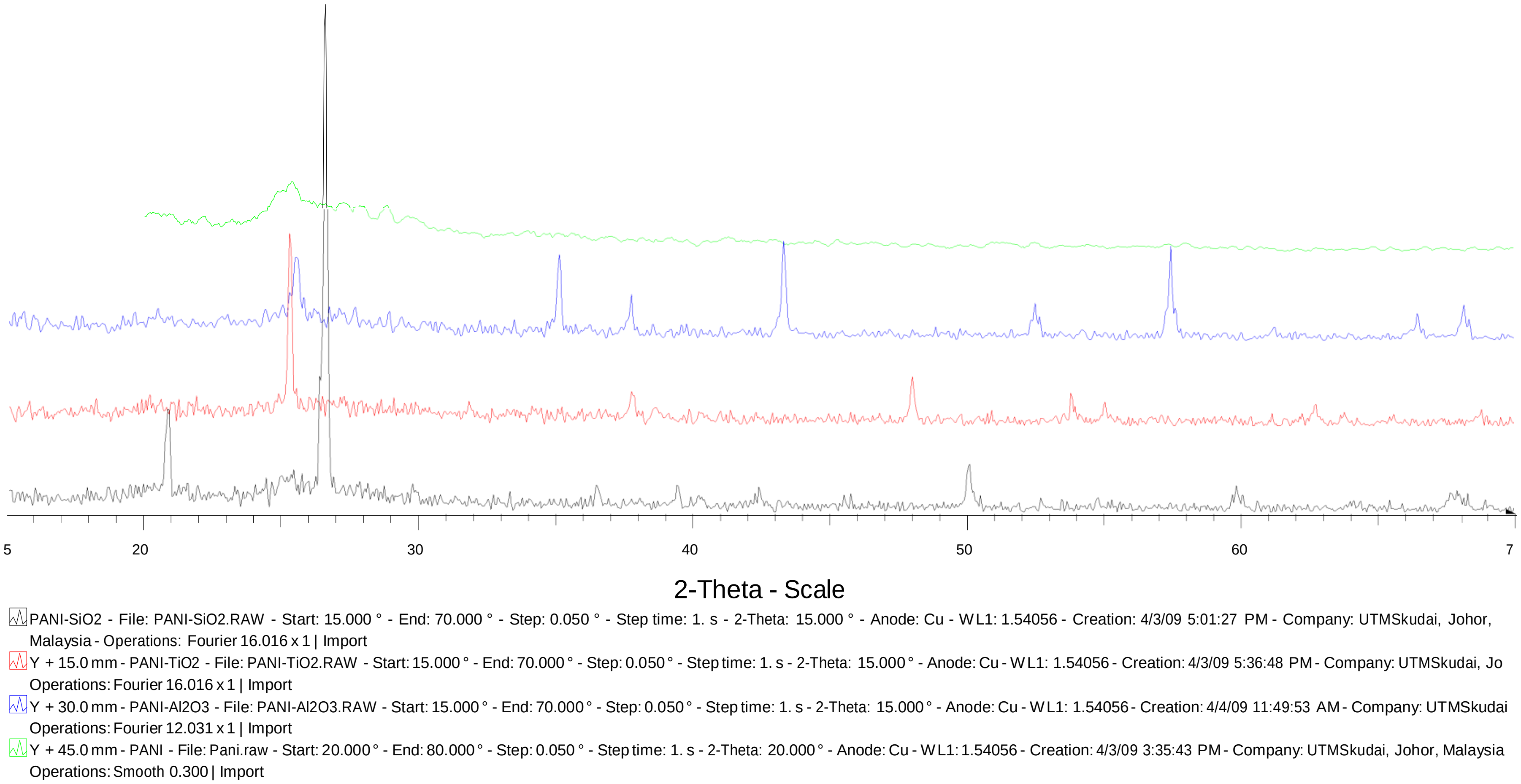


Figure 4.2: X-ray diffraction of PANI, PANI-Al_2O_3, PANI-TiO_2 and PANI-SiO_2 respectively

4.3 Pigments Morphology

4.3.1 Mechanism of PANI Nanostructures Formation Micelle Shapes

The PANI nanostructures were synthesized using aniline monomer doped by phosphoric acid and ammonium persulfate as oxidant agent. The PANI had been polymerized using phosphoric acid doped at increasing quantities with constant quantity of aniline monomer 1 M aniline and oxidant agent 1 M ammonium per sulfate (0.1:1, 0.5:1, 1:1 and 2:1 M). The reaction was allowed to proceed for 6 h at 0-5 °C After the reaction time, the product was filtered and washed with water followed by acetone. Then the product was dried in oven at 50° C for 24 h.

Recently, nanoscale attract many attention in conductive polymer fields especially with polyaniline applications: such as :Nanoparticles (Li and Kaner. 2006). Nanotubes (Wei *et al*., 2002), (Zhang et al., 2005) and (SHEN, and WAN,1999).Nanospheres (Wei and Wan ,2002). Nanowires (Liu *et al*., 2004). Nanofibers (Huang *et al*., 2003), (Huang, and Kaner.,2004) and (Virji *et al*., 2004).

Usually, PANI nanostructure with controllable morphology have been synthesized by chemical oxidative polymerization of aniline with the aid of surfactant which is act as template for nanostructure formulation such as sodium dodecyl benzene sulfonate (SDBS) (Li *et al*., 2006), (Zhang *et al*., 2002) or sodium dodecyl sulfate (SDS) (Hassan *et al*., 2002) (Hassan *et al*., 2004) (Zhang *et al*., 2007) (Kim *et al*., 2001) and (Kim *et al*., 200).

Some author's chose suitable surfactant obtained two actions (template and dopant) at one time Such as: Molybdic acid (Zhang *et al*., 2008) β-naphthalene sulfonic acid (Wei *et al*., 2002), (HUANG and WAN, 1999), Azobenzenesulfonic acid (Huang *et al*., 2003) and selenios acid (Amarnath *et al*., 2008). It was determined that the nano formation of PANI was strongly dependent on the dopant-monomer mole ratio. For example, Polyaniline nanostructures changed up to molar ratio between the monomer and dopent Aniline-H_3PO_4. Amarnath *et al*. (2008) structure-directing agents like hydrophobic/hydrophilic dyes and surfactants were not utilized and only phosphoric acid dopant for synthesizing the well ordered PANI nanofiber and nanorods was used. Xia *et al*. (2005) reported the synthesis of ordered PANI nanorods using hydrophilic (Allura Red AC) as the structure-directing agent and that the formation of ordered arrays was due to the formation of rod shape like micelle aggregates and utilized structure-directing agents (surfactant and dyes) and dopants.

Table 4.3 Effect of doped-monomer ratios on PANI nanosizes

Average Diameter	Nanostructure	Doped Con.	Monomer Con.
25-33 nm	Nanosphere	H_3PO_4 2M	Aniline 1M
25-33 nm 28-40 nm	Nanosphere + Nanofiber	H_3PO_4 1M	Aniline 1M
155-165 nm	Nanoroad	H_3PO_4 0.5M	Aniline 1M
25-50 nm	Nanofiber	H_3PO_4 0.1M	Aniline 1M

In this research, aniline was mixed with the phosphoric acid solution; the phosphoric acid-aniline (dopant-monomer) was formed through an acid/base reaction. The (dopant-monomer) can form micelle-like arrangements, acting as templates to form nanostructures under certain conditions as shown in Fig. 4.3. In (dopant-monomer) the phenyl ring acts as a hydrophobic and $H_2PO_4^-$ as hydrophilic and this enhance forming of micelle-like arrangement. Once the molarities of H_3PO_4 (hydrophilic) double aniline monomer (hydrophobic) molarities the nanostructures turn to be sphere micelle. When the molarities ratios is opposites, aniline monomer double acid doped H_3PO_4 nanostructures of polyaniline turned to be nanocylinder form. As well as ratios of aniline-phosphoric acid (1: 0.1) produce polyaniline nanofiber also cylinder form means, PANI nanostructures the diameter of cylinder form turned to Decrease when the molarity of Dopant decreases (Zhang *et al.,* 2002).

Once the ratio of hydrophilic phosphoric acid molarities double of hydrophobic aniline monomer, most of aniline molecules were complexes protonated with phosphoric acid to form the sphere shaped micelles and there is very few aniline molecules free to diffuse into Aniline-Phosphoric acid micelle And $H_2PO_4^-$ surrounding the PANI tail (Yoon, 2008).

When the ratio of hydrophilic phosphoric acid molarities half of hydrophobic aniline monomer, few aniline molecules were protonated with phosphoric acid and more free aniline monomer were not complexed. This free aniline diffused into the Aniline-Phosphoric acid micelles then elongating the micelles to form cylinder form micelles. These cylinder form micelles after polymerization produce PANI nano cylinder nano road forms (Wei *et al*., 2002).

While decreasing the ratios of aniline-phosphoric acid to (1 - 0.1) resultant PANI nano fiber means, when decrease the ratios of doped the diameter cylinder will decreases and once the decreasing of acid doped produce more free aniline monomer which is not protonated , free aniline monomer not protonated decrease the diameter for PANI nan cylinder.

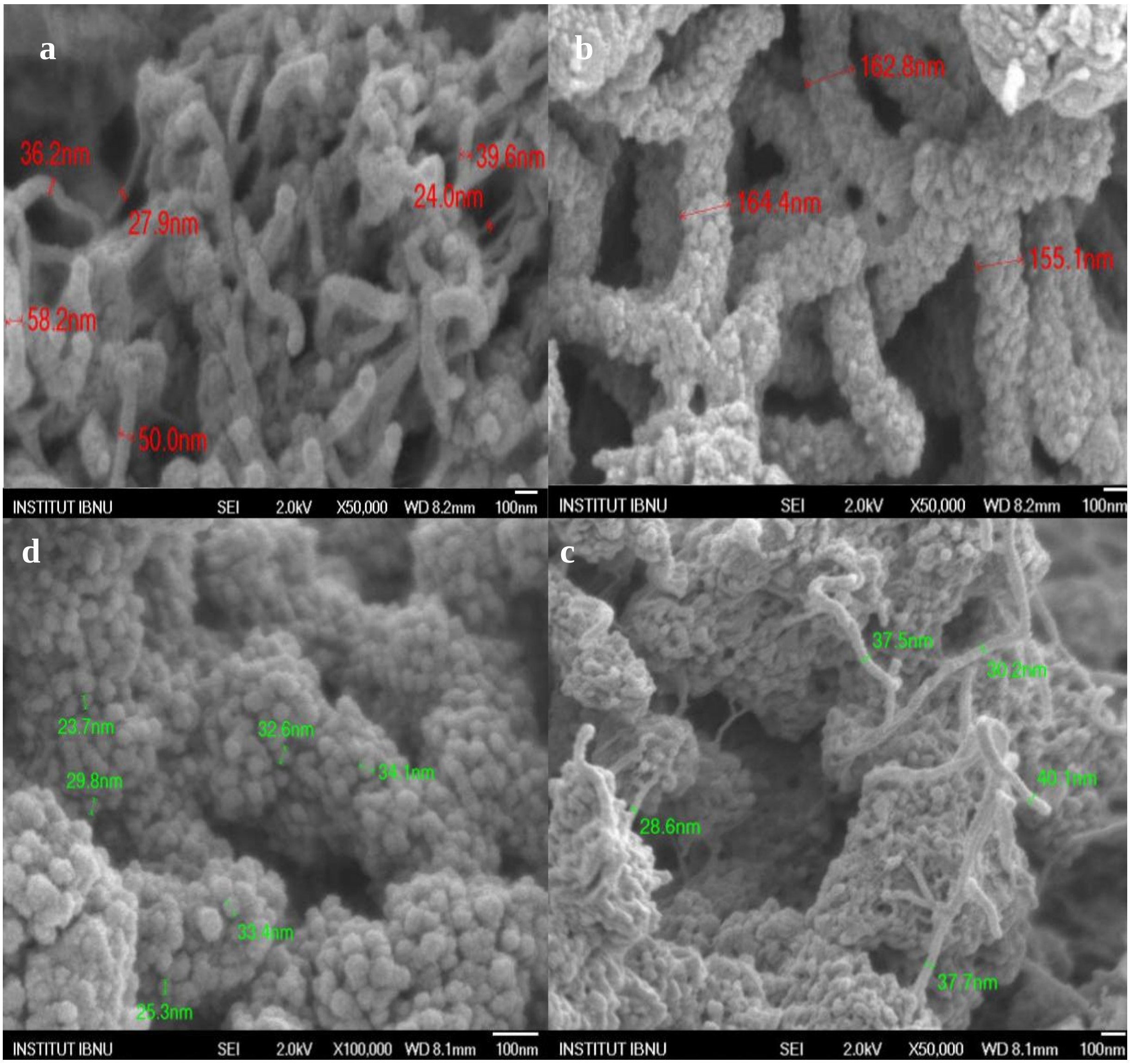


Figure 4.3 FE-SEM images of PANI morphology nanostructures (a) Nanofiber, (b) nanoroad, (c) Mix of Nanofiber, nanosphere and (d) Nansphere PANI.

A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single tail regions in the micelle centre. Micelle phases including: shapes such as sphere, cylinders, and bilayers are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength.

Surfactant is wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. The term surfactant is a blend of **surf**ace **act**ive **a**ge**nt**. Surfactant is usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water.Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC (Yoon, 2008).

The process of forming micelle is known as micellization and forms part of the phase behavior of many lipids according to their polymorphism (Baeurle and Kroener, 2004).The molecule must have a strongly polar "head" and a non-polar hydrocarbon chain "tail". When this type of molecule is added to water, the non-polar tails of the molecules clump into the center of a ball like structure called a micelle, because they are hydrophobic or "water hating". The polar head of the molecule presents itself for interaction with the water molecules on the outside of the micelle.

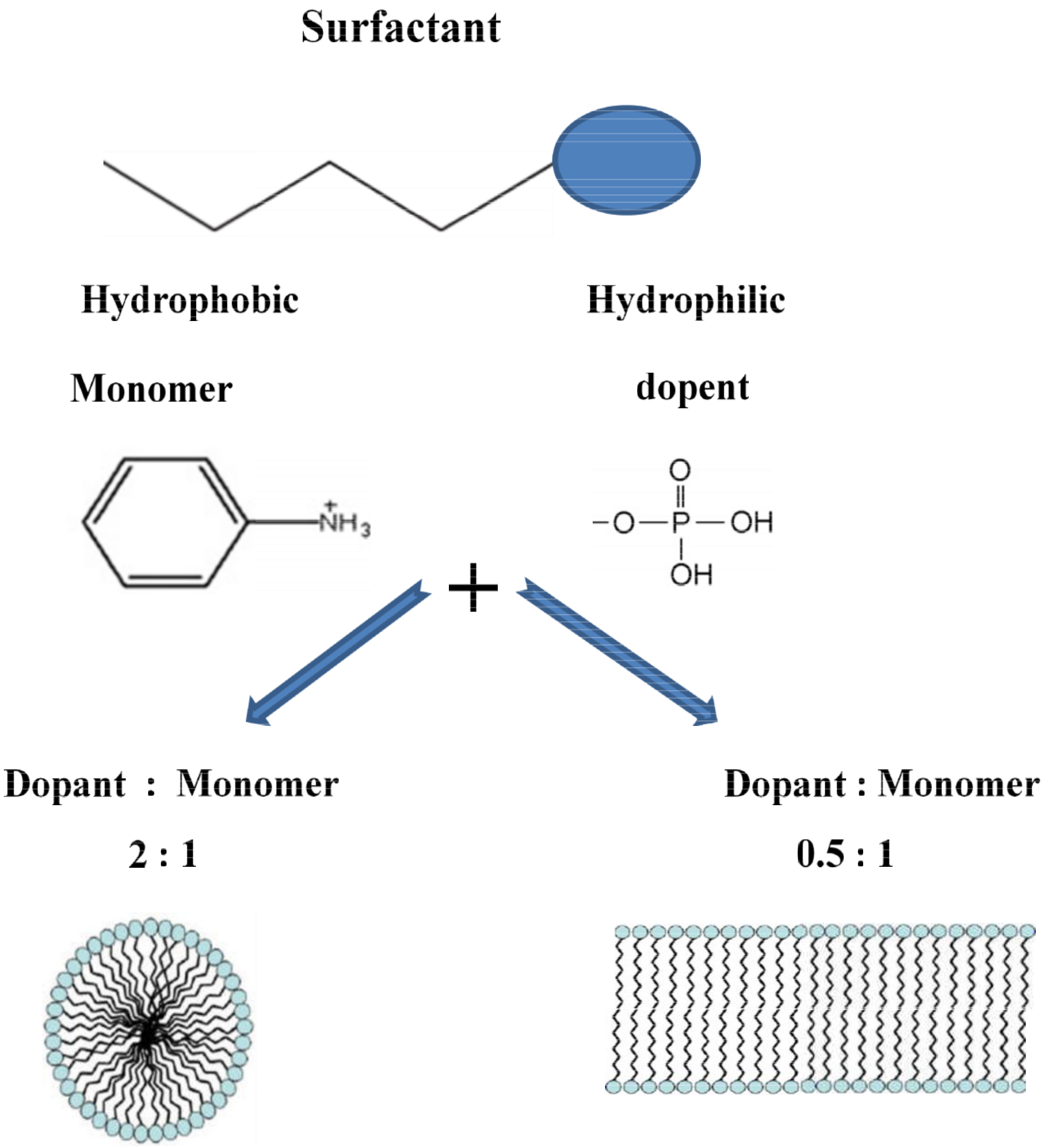


Figure 4.4 Mechanism for the formation of PANI nanostructures (Rod or sphere) shaped micelle.

4.3.2 Morphology of PANI Composites with (Al_2O_3, SiO_2 and TiO_2)

In situ polymerization with dropwise addition of the (APS) solution into the (Al_2O_3,SiO_2 and TiO_2) powders containing aniline doped dispersions, the color of three dispersions changed from the milk white to green, then dark green, implies formation of PANI. All the powders were coated with PANI, indicating that ANI was preferentially polymerized at the surfaces of the powders. This phenomena has been reported previously by Wan (1989) The initially formed oligoaniline cation radicals would be adsorbed on the insulating surfaces and the coupling reaction and enhancing polymerization would begin from these nucleation sites, instead of from the bulk as mention in micelle, leading to the preferentially formed adherent PANI layer on the Surfaces, If there is more ANI is presented in reaction , the secondary nucleation would occur on the produced thick layer PANI layers with particulate appearances. Polyaniline composite with (Al_2O_3, SiO_2 and TiO_2) was successfully prepared by the oxidative polymerization of aniline in the presence of amorphous Al_2O_3, SiO_2 flake particles and amorphousTiO_2 sphere particles.

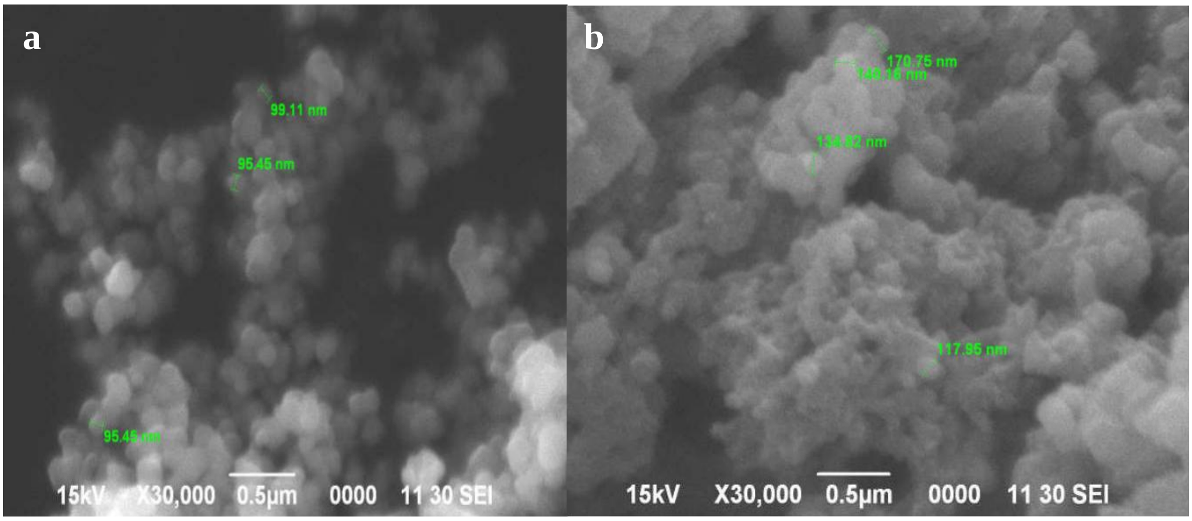


Figure 4.5 SEM (a) TiO_2, (b) PANI-TiO_2 composite

Clearly Figure 4.6 shows the size of TiO_2 particles had been increase because of the polyaniline layer which is deposited on the surface of particles TiO_2.Metal oxide is has surface positive charge. In acidic conditions $H_2PO_4^-$ ions adsorbed by positive charge on the Metal oxide surface. ANI monomers are converted to Anilinium cations in acidic conditions. Electrostatic interactions occur between anions adsorbed on the metal oxide surface and anilinium cations. The ANI monomers combine electrostatically with Metal oxide nanoparticles and then Polymerised with increasing molecular weight of the polymer (Li *et al.*, 2008).

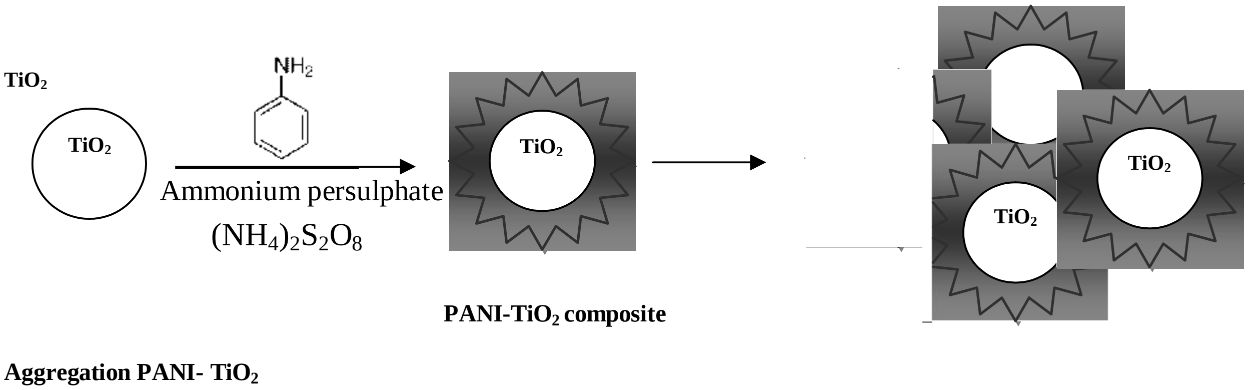


Figure 4.6 Synthesis PANI-TiO_2 composite

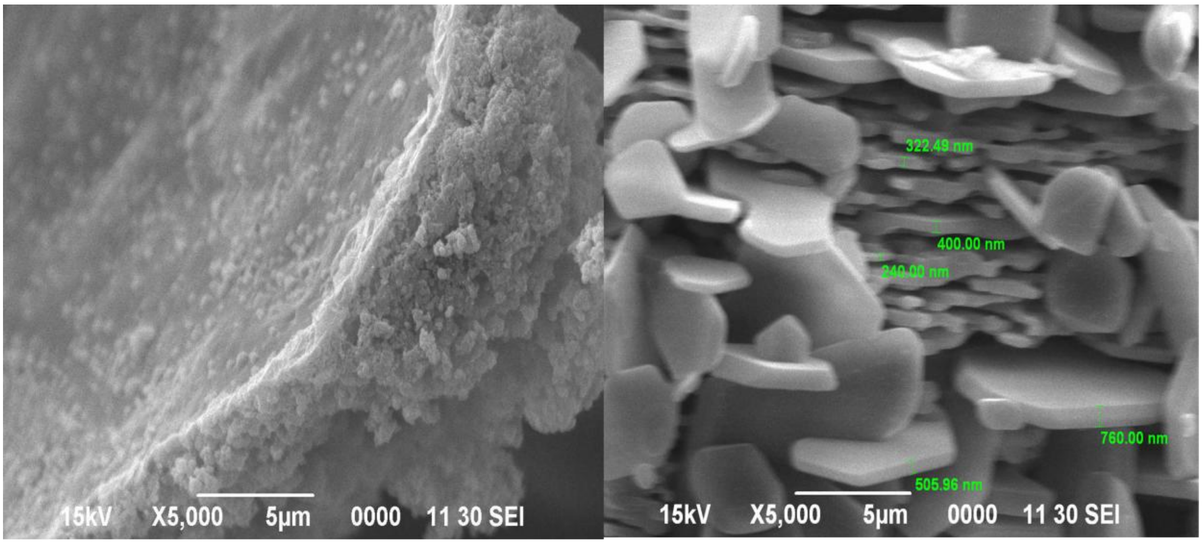


Figure 4.7 SEM (a) Al_2O_3, (b) PANI- Al_2O_3 composite

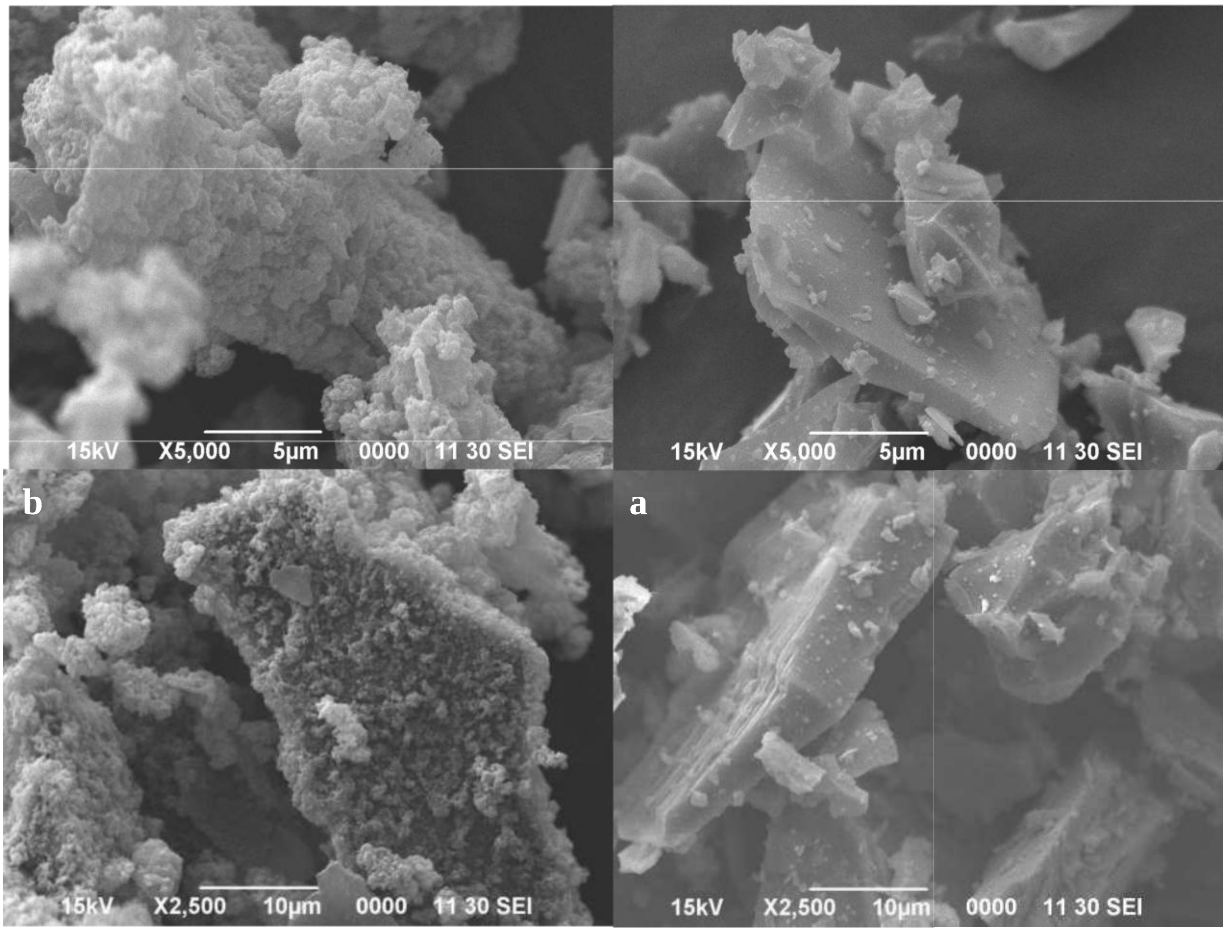


Figure 4.8 SEM (a) SiO_2, (b) PANI-SiO_2 composite

SEM shows the flake particles of SiO_2 and Al_2O_3 before and after coated with polyaniline and Polyaniline almost fully encapsulated the flake particles Figure 4.7 and Figure 4.8 Otherwise polyaniline nanoparticles deposited on surface of flakes. In that case, the composite materials consider as new hybrid materials which has new properties exist neither polyaniline nor inorganic particles.

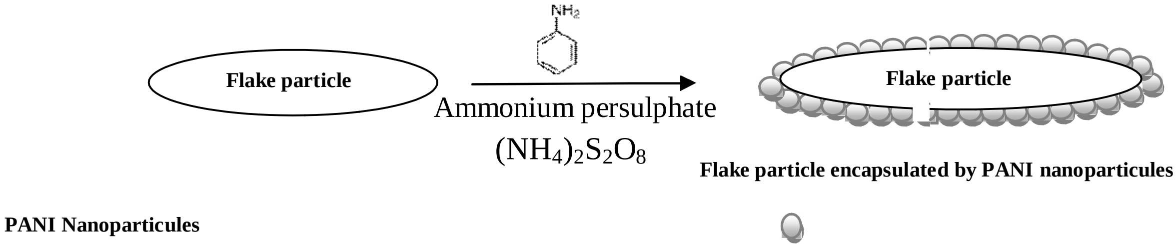


Figure 4.9 PANI composite with flake particles

4.4 Conductivity

The conductivity of seven pigments has been measured using digital Multimeter through measured pigments resistance then converted to conductivity by equation. The resistance was taken for ten deferent points of each pigment. The powders were pressed into a pellet of 1.29 cm diameter and 0.19 cm thickness under pressure. The conductivity measurement of pigments pellets was measured at room temperature. Samples were dried in vacuum before making into pellets. The conductivity collected through measuring the pellets resistance and applies equation below:

$$\text{Conductivity (S/cm)} = \frac{1}{\text{Resistance}(\Omega)} \text{ / diameter (cm)} \tag{4.1}$$

Table 4.4 Pigments conductivity

Sample	Morality of H_3Po_4 doped	Resistance (Ω)	Conductivity(s/cm)
PANI	0.1 M	2.92	0.27
PANI	0.5 M	1.15	0.67
PANI	1 M	0.61	1.27
PANI	2 M	0.67	1.15
PANI-TiO_2	1 M	0.87	0.90
PANI-SiO_2	1 M	0.25	3.0
PANI-Al_2O_3	1 M	0.40	1.94

The differences in conductivity may be due to the lower dopant concentration or different material composition. In case of polyaniline alone, the morphology of the nanorods significantly affected the conductivity.

Less dopant was used to synthesize crystalline PANI nano cylinder with a good conductivity. It is also clear from the nano cylinder FE-SEM image that a good conductive network was formed, therefore indicating that compared to the amount of dopant used, The behavior suggests that the morphology it is the important factors in terms of conductivity of PANI nanostructures, It has more effect on conductivity. The correlation of PANI morphology compared betweens nano cylinders forms the high conductivity is PANI nanorods because of has widest diameter than nanofiber. Further, diameter and conductivity increases with increasing of dopend ratios until equality betweens monomer and doped (nanosphere particles) then continue almost consistent. Furthermore, there is no consistent relationship between doped-monomer ratios and conductivity. In case of PANI composite clearly we can see the PANI composite with flake particles such as Al_2O_3 and SiO_2 save the heights conductivity more than sphere particles TiO_2 especially PANI-SiO_2 , save the highest conductivity maybe because of semiconductor behavior of silicon which is support PANI conductivity as well as supporting material in case of batteries application.

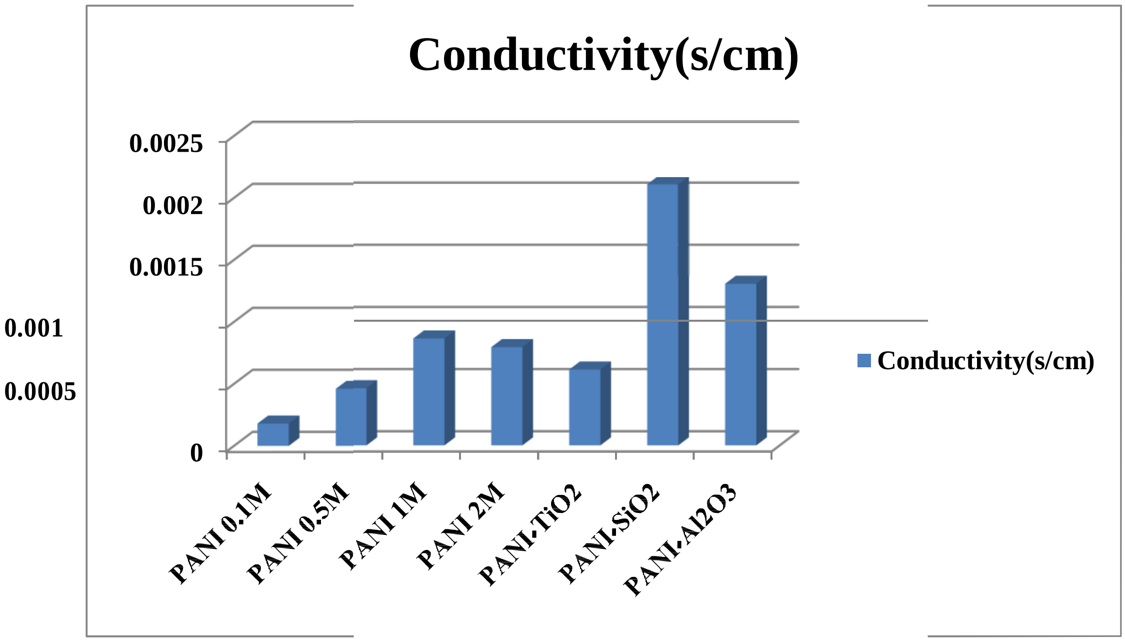


Figure 4.10 Average of pigments conductivity

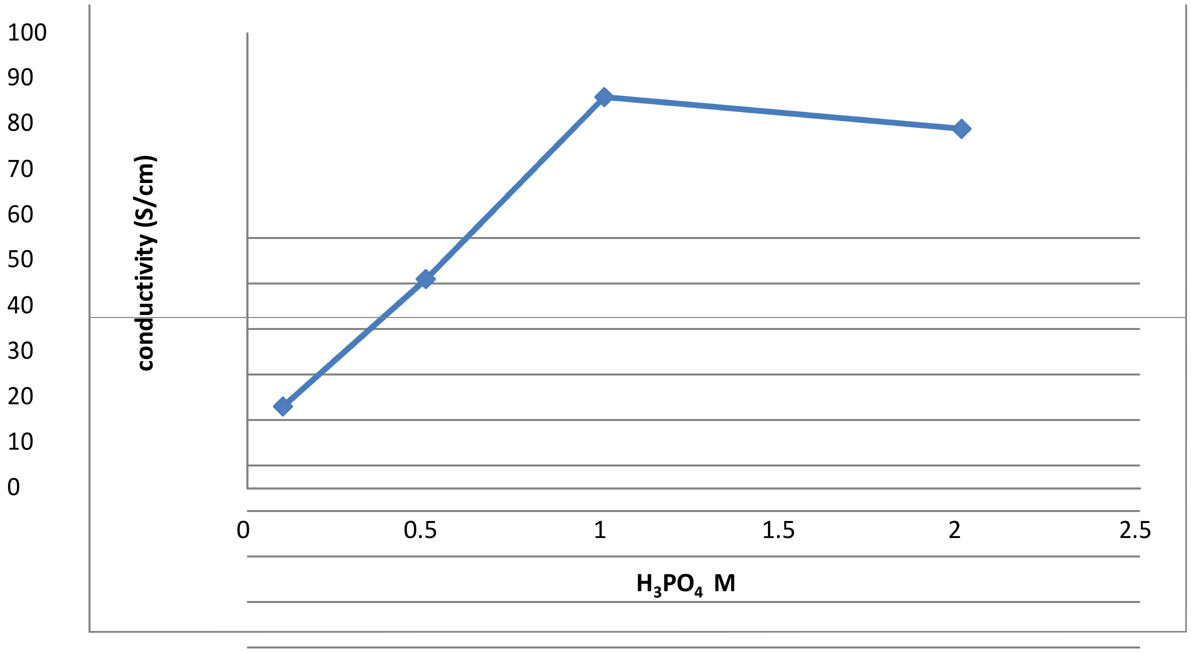


Figure 4.11 Conductivity (S/cm) for PANI by changing doped ratio

4.5 Dispersion Stability

Fig.4.11 shows the dispersion stability of PANI with four different nanostructures at increasingly periods. Once PANI dispersion by ultrasonication in ethanol stopped, the dispersion stability test had starting until 24 hours stopping the stirring action. PANI nanofiber has the best dispersion stability (Yao et al. 2008) follow by nanoroad, mix nanofiber nanosphere and nanospher. PANI nanospheres have worst dispersion stability in terms of faster precipitating before 1 hour follow by the PANI mixture nanosphere and nanofiber which is started participating during first three hours. PANI nanorod start precipitates after six hours of beginning of test and not participated completely while the PANI nanofiber stable with never precipitates in ethanol medium.

These results extracted PANI in cylinder nanostructures have very good dispersion stability And this dispersion stability increase when the diameter for cylinder decreases.

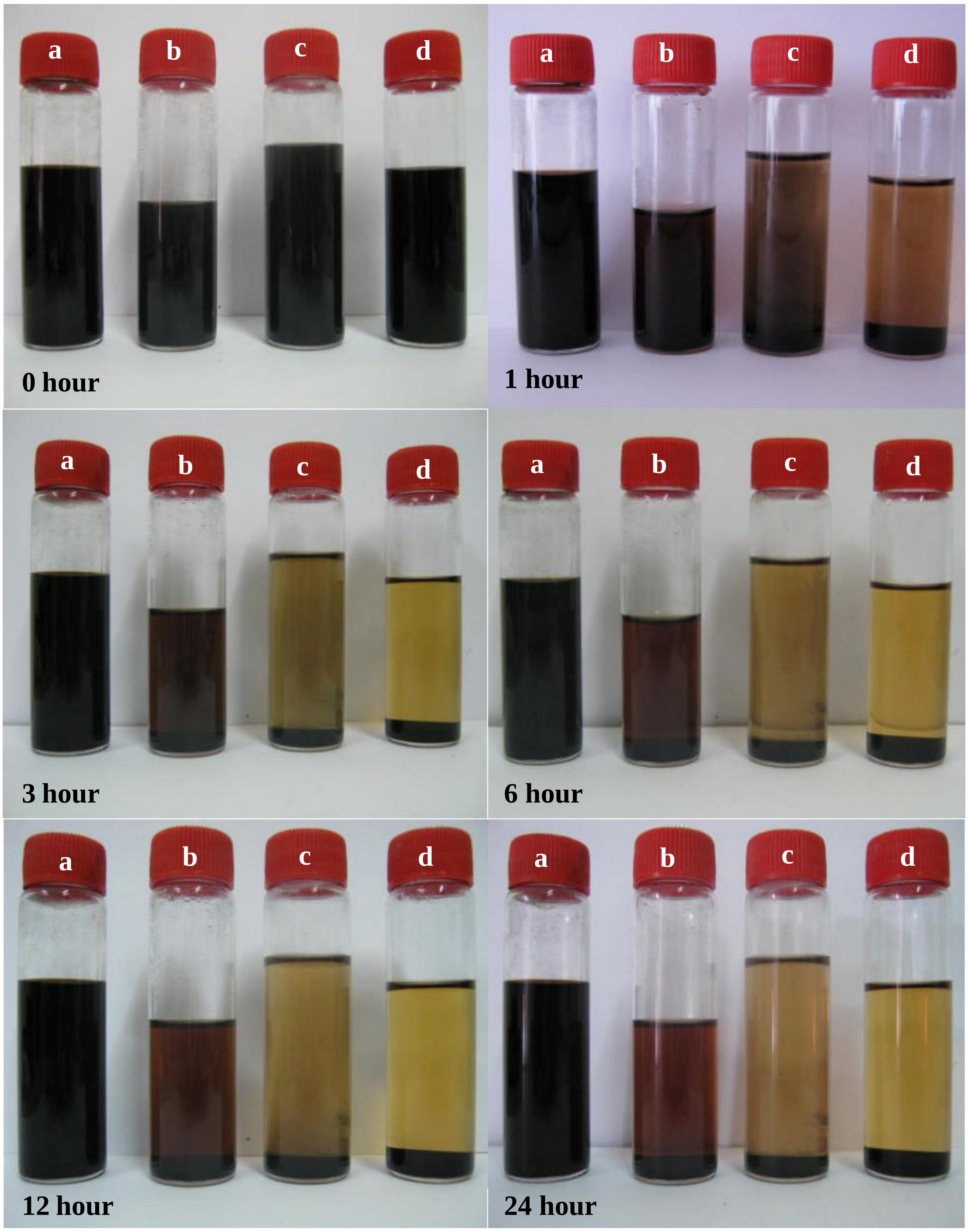


Figure 4.12 Dispersion stability for PANI with different nanostructures; sample (a) nanofiber, sample (b) nanoroad, sample (c) mix nanofiber and nanospher, Sample (d) nanosphere

4.6 Corrosion Evaluation

4.6.1 Immersion Test

Seven pigments have been exposed to immersion test evaluation according to ASTM G31 standard. Corrosion investigation by fully immersion test in 5% NaCl solution over 1440 hour for seven pigments each one has five sample. Samples were taking out at the end of exposure periods, and removed the coating then calculate the mass loss for each specimen. The results of average mass loss are described in Tables 4.5:

4.6.1.1 Corrosion Rate

According to ASTM G31 standard the size and the area of specimens were consider and the corrosion rate calculated used corrosion rate equation which written below:

$$\text{Corrosion Rate} = \frac{K \times W}{A \times T \times D} \qquad (4.2)$$

K = a constant, *T* = time of exposure, *A* = area in cm^2, *W* = mass loss, *D* = density

$$A = \pi / 2(D^{2\ -}\, d^{2}) + t\pi D + t\pi d \qquad (4.3)$$

Where: *t* = thickness, *D* = diameter of the specimen, and *d* = diameter of the mounting hole.

Table 4.5 shows average of mass loss and corrosion rate for each pigment used in corrosion protection in immersion test technique. Generally, corrosion rate increase with increase in mass loss, PANI-SiO_2 has less mass loss corrosion rate during the periods of exposed. Either because of its high conductivity which is supports the pigments for absorbing the aggressive ions or physical flack formulation of PANI-SiO_2 which impedance permeability of aggressive ions through coating to substance.

In case of PANI with three different nanostructures, they have almost same corrosion rate except polyaniline nanoroad which is doped by 0.5M phosphoric acid. Probably the hole between nanoroad shapes increases the permeability of aggressive ions through coating which influence coating passivity or due to high diameter nanosize (155-165nm) once nanosize increase surface area decrease.

Table 4.5 Corrosion rate for organic coating

pigment used in coating	Acid dopant Molar ratio	average of samples mass loss (g)	Corrosion rate ($g/m^2 \cdot h$)
Barer samples	non	0.47 g	3.263
PANI	0.1 M	0.048 g	0.333
PANI	0.5 M	0.087 g	0.608
PANI	1M	0.049 g	0.34
PANI	2M	0.035 g	0.245
PANI-TiO_2	1M	0.068 g	0.472
PANI-SiO_2	1M	0.025 g	0.175
PANI-Al_2O_3	1M	0.027 g	0.19

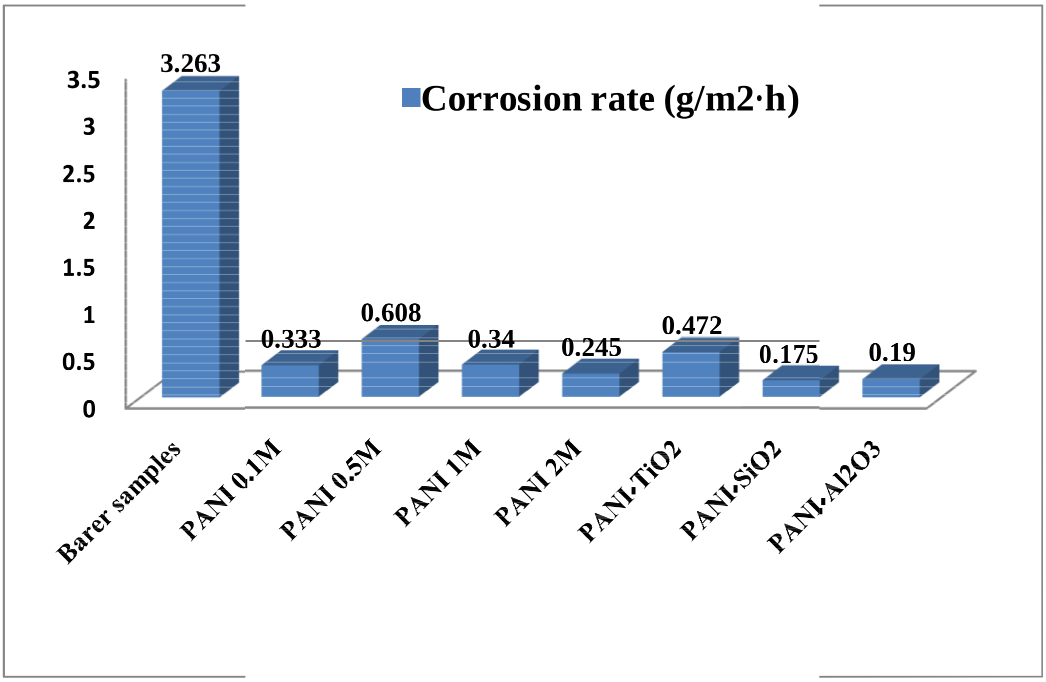


Figure 4.13 Corrosion rate

4.6.2 Salt Spray Tests

According to standard ASTM B117 coatings containing the seven pigments exposed in salt fog cabinet for 35 days, coating containing pigments were applied by brush in two layers and left to dry for 24 hours. After the coating has dried completely, samples were cracked in the middle using a sharp edge. Visually we can distinguish from Figure 4.14, the corrosive effect in the three composite pigments containing coating that is indicated to PANI-SiO_2 pigments can protect coating more than other two followed by PANI-Al_2O_3 then the PANI-TiO_2 respectively.

In terms of PANI nanostructures, best corrosion protection provided by PANI nanofiber followed by nanoroads then nanospheres respectively. This protectively provided by the higher dispersion stability which is supported disperses the PANI in each and every where in specimen. So, this ensures that the PANI nanofiber distribute very well in two side of the crack edges which is achieves our aims by Reducing the rate of aggressive ions permeability to the metal.

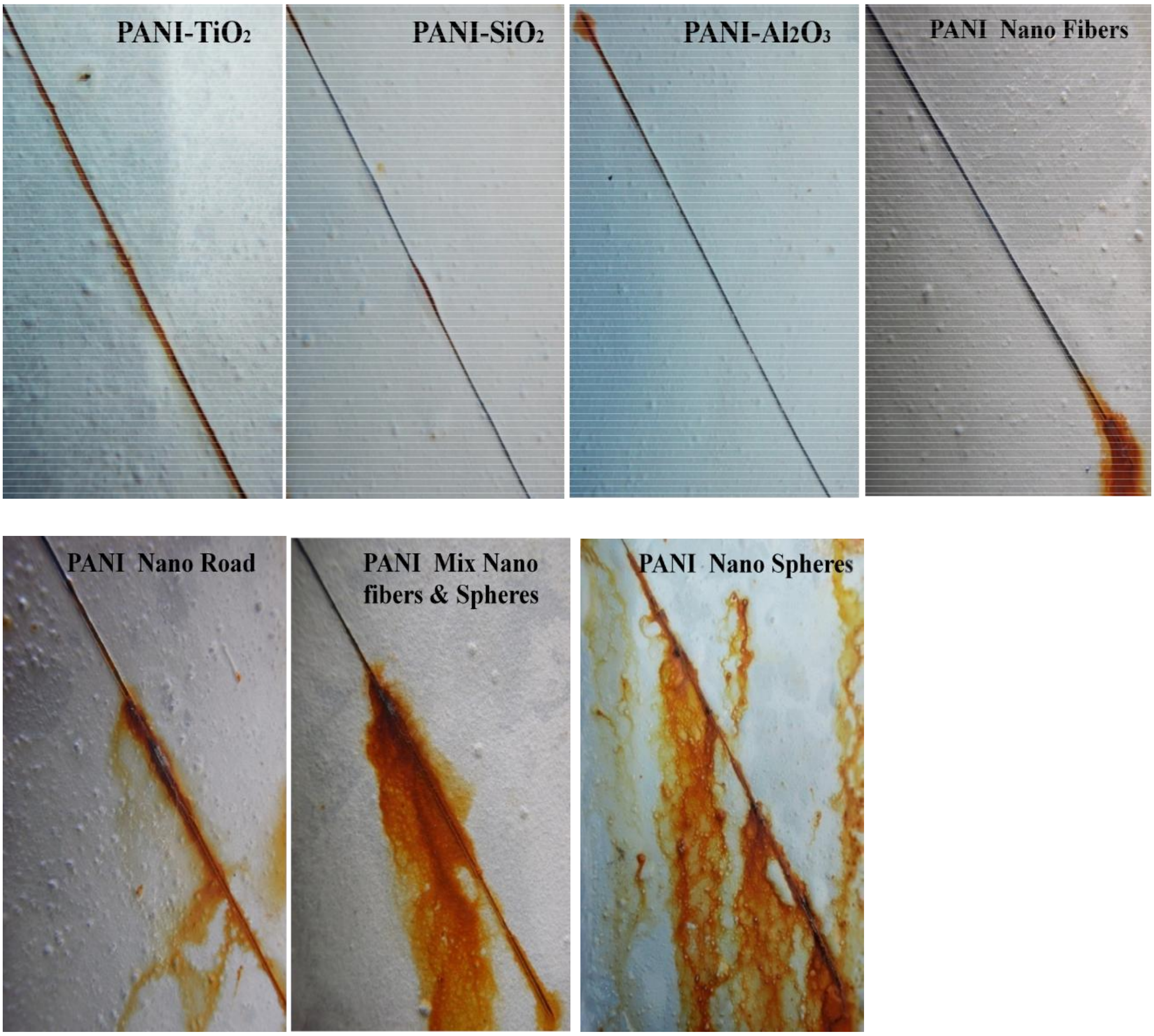


Figure 4.14 Salt spray samples after 35days exposed

4.7 Adhesion and Thickness Tests

After the completion of the salt spray exposure period, samples were carried out for adhesion test according to ASTM D3359 standard. Table 4.6 shows the average coating thickness according to ASTM D1186 standard and adhesion test according to ASTM D3359 standard (the higher value of adhesion is 5B and the lower one is 0B). Adhesion and thickness tests were carried out at STATUS HEAD Company (Johor-Malaysia). The average of thickness test was taken from different ten places for each sample then lower and higher thickness had been listed in Table 4.6. The adhesion test was taken through making seven horizontal scratch lines cross with other vertical lines in order to produce thirty-six squares in the coatings. These squares were under appropriately pull-up motion by special tape. Pull-up adhesion tests were done in five different areas in each sample. Thickness test was taken from different ten places in sample then lower and higher thickness had been listed in table below.

Table 4.6 Averages of thickness an adhesion tests

pigment	average of coating Thickness (Micron)	Average of adhesion test
PANI nanofiber	207-227	4B
PANI nanorod	214-223	5B
PANI mix forms	238-292	5B
PANI nanosphere	234-293	3B
PANI-TiO_2	335-340	5B
PANI-SiO_2	246-339	5B
PANI-Al_2O_3	290-330	5B

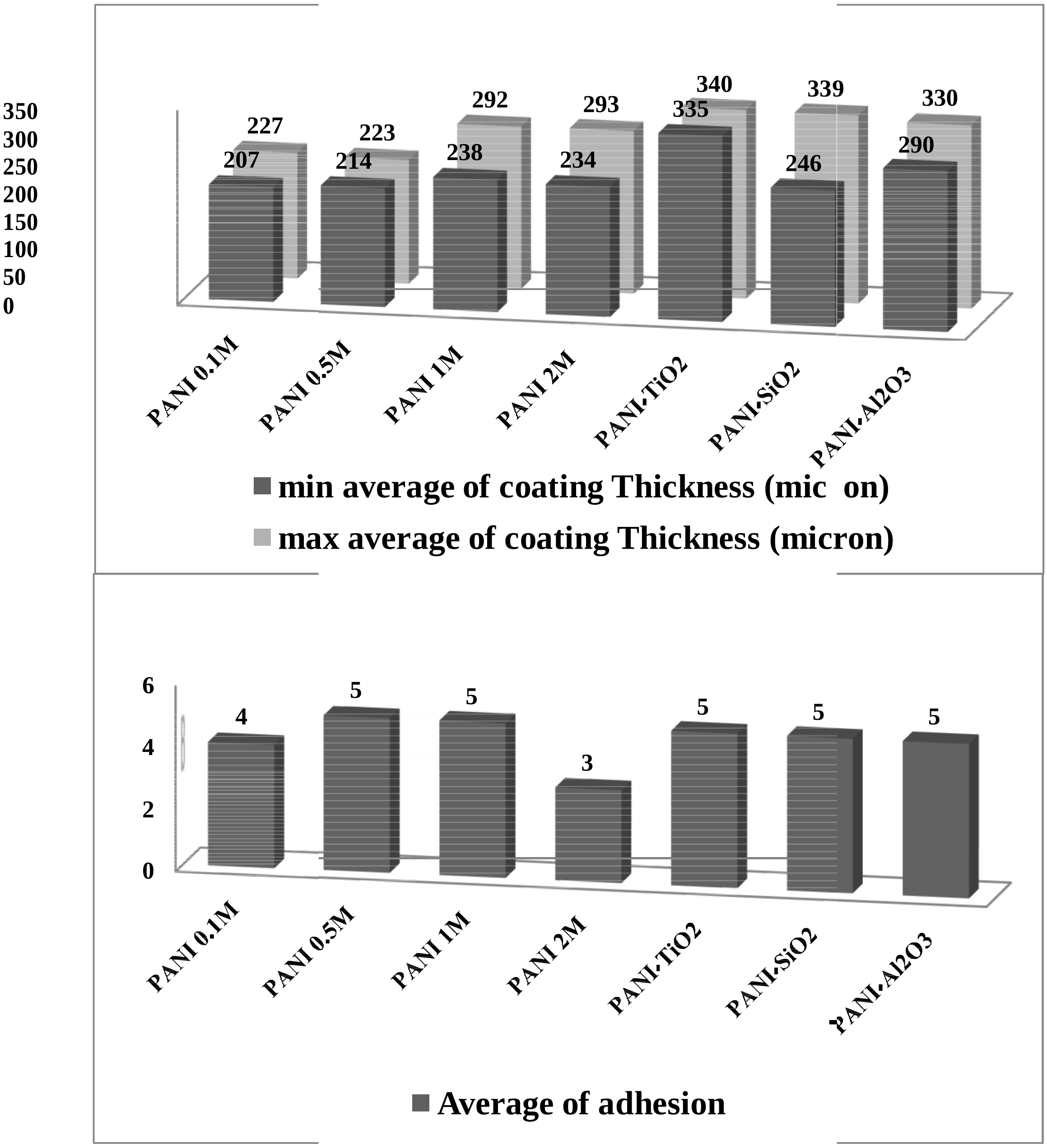


Figure 4.15 Averages of thickness an adhesion tests

Results of Figure 4.7 describe the seven samples coated with seven pigments almost have the hig~~hest value of adhesion test with different co~~ating thickness and almost no effect for adhesion efficiency. Except of PANI nanofiber slightly affected for adhesion test 4B, probably the thickness of coating which is has the less thickness.

On the other hand, PANI Nanosphere pigment containing coating had the lowest value of adhesion test 3B among the three pigments. The authors believe that this is due to the bad corrosion protection ability of PANI Nanosphere, which results in the production of rust between the surfaces, in turn this causes the delamination of coating by pushing the coating up which leads to the decrease of the adhesion value (Zarras *et al*. (2003) and Armelin *et al*. (2008)).

The anticorrosive coatings pigmented with an flake pigment shows excellent barrier properties(Sathiyanarayanan *et al.,*2007b) .They hinder the permeation of corrosive substances through the film flake pigmented coatings are a more efficient barrier (Qi *et al.***,**2008).for water vapor and aggressive ions than the isometric spherical particles pigmented coatings(Fahlman et al., 1997). It works to disrupt and prolong the path to substance against aggressive substances show fig 4.9.

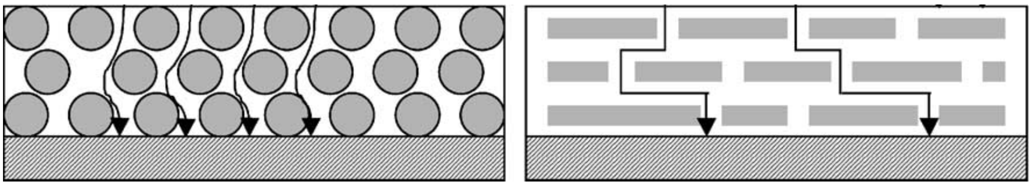


Figure 4.16 Path of aggressive ions through coating to the metal

Our special two flakes pigments have shown high efficiency in terms of protecting. Pigments possess the important and effectively factors for corrosion Protection in organic coating. Firstly, maybe disrupted and prolonging the path of corrosive substances to metal by it is flake shape. Secondly, because the surface of SiO_2 and Al_2O_3 flakes had been coated by PANI doped with phosphoric acid, which could have form passive film by releasing ions of phosphate by PANI-ES and become PANI-LS then form iron–phosphate complex as well as PANI-LS, which is able to re-oxidize to PANI-ES by the dissolved oxygen present in the medium.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Conductive polymers have a wide application in terms of corrosion protection. Current work focused on producing new PANI anticorrosion pigments such as nanoroad, nanosphere and nanofiber as well as new metal oxide composited with PANI such as SiO_2 and Al_2O_3.However, The anticorrosion properties of the polyaniline prepared using situ polymerization with three different nanoforms and PANI composite with SiO_2 and Al_2O_3 have never been reported based on authors' knowledge. The Results of this work concluded:

1. PANI composites with three inorganic oxides pigments and three different nanostructures by situ polymerization were successfully synthesized.
2. Phosphoric acid work as template and doped as the same time and produce three different nanostructures with changing the monomer-acid doped ratios.

3. PANI-SiO_2 gives the highest conductivities compared with three composite pigments.
4. Conductivity increase with increasing of ratio of phosphoric acid doped till equal amounts then continue constant.
5. Nanofiber is the best dispersion stability among three nanostructures pigments.
6. PANI-SiO_2 pigment shows excellent anticorrosion properties in full immersion test. However, PANI with three different nanostructures have almost similar anticorrosion properties.
7. The pigments offered good corrosion protection in salt spray test except PANI Nanosphere. However, the adhesion strength is decreases with increasing of corrosion in coating.

5.2 Future Work

The potential use of carbon nanotubes and nanofibers as smart composite materials is discussed future work. The properties of carbon nanotube materials will be study, and then four possible applications under development will be discuss. The first application is electrochemical actuation in dry and aqueous environments. The second is a carbon nanotube polymer piezoresistive strain sensor developed for structural health monitoring. Third, nanotubes are usedwith an electrolyte for harvesting power from structural vibration. Fourth, a carbon nanotube bioelectronic sensor. Study all this applications together and using nanoscale smart materials to synthesize intelligent electronic structures with prescribed elastic and electrical properties for a wide range of new applications.

REFERENCES

Abdiryim, T., Xiao-Gang, Z. and Jamal, R. (2005). Comparative studies of solid-state synthesized polyaniline doped with inorganic acids, *Mater. Chem. Phys* 90:367–372.

Abu, Y. M. and Aoki, K.(2005).Corrosion protection by Polyaniline-coated latex microspheres. Journal of Electroanalytical Chemistry.583: 133–139.

Akbarinezhad, E., Ebrahimi, M. and Faridi, H.R. (2009). Corrosion inhibition of steel in sodium chloride solution by undoped polyaniline epoxy blends coating.*Progress in Organic Coatings* 64:361–364.

Alam, J., Riaz, U. and Ahmad, S. (2009). High performance corrosion resistant polyaniline/alkyd ecofriendly Coatings. *Current Applied Physics* 9:80–86.

Ansari, R. and Alikhani A.H. (2008).Application of polyaniline/nylon composites coating for corrosion protection of steel. *Journal of Coating & Technology Research* 6 (2) 221–227.

Armelin, E., Aleman, C. and Iribarren , J. I. (2009) Anticorrosion performances of epoxy coatings modified with polyaniline: A comparison between the emeraldine base and salt forms. *Progress in Organic Coatings*.65 (2009)88–93.

Armelin, E.; Pla, R.; Liesa, F.; Ramis, X.; Iribarren J. I. and Alemán C. (2008) Corrosion protection with polyaniline and polypyrrole as anticorrosive additives for epoxy paint. *Corrosion science*, 50: 721-728.

Armelin, E., Oliver, R., Liesa, F., Iribarren, J., Estrany, F. and Alem´an, C. (2007) Marine paint fomulations: Conducting polymers as anticorrosive additives. *Progress in Organic Coatings* 59: 46–52.

Azim, S. S., Sathiyanarayanan, S., and Venkatachari, G.(2006).Anticorrosive properties of PANI–ATMP polymer containing organic coating. *Progress in Organic Coatings*, 56: 154–158.

Baeurle, S. A. and Kroener, J.(2004) Modeling effective interactions of micellar aggregates of ionic surfactants with the Gauss-core potential. *Journal of mathematical Chemistry 36:* 409–421.

Bierwagen, G. P. (1996) Reflections on corrosion control by organic coatings. *Progress in Organic Coatings* 28:43-48.

Bin Yao, Gengchao Wang, Jiankun Ye and Xingwei Li.(2008). Corrosion inhibition of carbon steel by polyaniline nanofibers, *Materials Letters* 62:1775–1778.

Cao, Y.; Li, S.; Xue, Z. and Guo, D. (1986) spectroscopic and electrical characterization of some aniline oligomers and polyaniline. *Synthetic Metals, 16* (1986) 305 – 315.

Chen,Y. ,Wang, X.H. , Li,J. ,Lu , J.L. and Wang, F.S.(2007). Polyanilin Forcorrosion prevention of mild steel coupled with copper. *Electrochimica Acta* 52:5392–5399.

Deberry, D.W. (1985) Modification of the Electrochemical and Corrosion Behavior of Stainless Steels with an Electroactive Coating. *Journal of Electrochemical Society132:*1022-1026.

Dey,A., De,S., De,A. and De, S. K. (2004) Characterization and dielectric properties of polyaniline–TiO_2. nanocomposites. Nanotechnology 15:1277–1283.

Dominis, A. J., Spinks, G. M. and Wallace, G.G. (2003).Comparison of polyaniline primers prepared with different dopants for corrosion protection of steel. *Progress in Organic Coatings* 48: 43–49.

Du, X.S., Xiao, M. and Meng, Y.Z.(2004). Facile synthesis of highly conductive polyaniline/graphite nanocomposites. *European Polymer Journal*, 40:1489–1493.

Dutta, K. and De, S.K. (2006) .Transport and optical properties of SiO_2–polypyrrole nanocomposites. Solid State Communications140:167–171.

Dutta, K. and De, S.K. (2007) Optical and electrical characterization of polyaniline–silicon dioxide Nanocomposite. Physics Letters A361:141–145.

Epstein, A.J.(1997). Electrically conducting polymers: *science and technology*. MRS Bull. 22 (6) 16–23.

Fahlman, M., Jasty, S. and Epstein A.J. (1997).Corrosion protection of iron/steel by emeraldine base polyaniline: an X-ray photoelectronspectroscopy study.Synthetic Metals.85:1323-1326.

Fenelon, A.M. and Breslin, C.B.(2005) Polyaniline-coated iron: studies on the dissolution and electrochemical activity as a function of pH . *Surface and coating technology* 190: 264-270.

Hassan, P. A. ; Raghavan, S. R. and Kaler, E. W. (2002) Microstructural Changes in SDS Micelles Induced by Hydrotropic Salt. *Langmuir* , 18: 2543-2548.

Hassan, P. A. ; Sawant, S. N. ; Bagkar, N. C. and Yakhmi J. V. (2004) Polyaniline Nanoparticles Prepared in Rodlike Micelles, *Langmuir* , 20: 4874-4880.

Herrasti, P and Oco´n, P. (2001). Polypyrrole layers for steel protection. *Applied Surface Science* 172:276-284.

Huang , K. and WAN, M. (2003) self-assembled nanostructure polyaniline Dopedwith Azobenzenesulfonic acid. *Synthetic metals,*135-136 :173-174.

Huang, J. ; Virji, S.; Weiller, B. H. and Kaner, R.B. (2003) Polyaniline Nanofibers: Facile Synthesis and Chemical Sensors. Journal American Chemical Society, 125:314-315.

Huang, J. and Kaner , R. B. (2004) A General Chemical Route to Polyaniline Nanofibers. *Journal American Chemical Society*, 126:851-855.

Huang, J. and WAN, M.(1999) In Situ Doping Polymerization of Polyaniline Microtubules in the Presence of β-Naphthalenesulfonic Acid. *Journal of Polymer Science: Part A: Polymer Chemistry*, 37:151–157.

Huerta-Vilca, D., De Moraes, S. R. and De Jesus Motheo, A. (2004). Anodic treatment of aluminum in nitric acid containing aniline, previous to deposition of polyaniline and its role on corrosion *Synthetic Metals,*140: 23–27.

Jadwiga Laska. (2004). Conformations of polyaniline in polymer blends. *journal of Molecular Structure,* 701:13–18.

Jianguo Wang. (2002). Anion exchange nature of emeraldine base (EB) polyaniline (PAn) and a revisit of the EB formula. *Synthetic Metals,132:* 49–52.

Kalendov´a, A., Sapurina, I., Stejskal, J.and Vesely, D. (2008) Anticorrosion properties of polyaniline-coated pigments in organic coatings. *Corrosion Science* 50: 3549–3560.

Kalendov´a, A., Vesel´y, D. and Stejskal, J. (2008). Organic coatings containing polyaniline and inorganic pigments as corrosion inhibitors. *Progress in Organic Coatings,* 62: 105–116.

Kalendov´a, A., Vesely ,D. , Sapurina, I. and Stejskal, J. (2008).Anticorrosion efficiency of organic coatings depending on the pigment volume concentration of polyaniline phosphate. *Progress in Organic Coatings* 63: 228–237.

Kalendova, A., Vesely, D., Stejskal, J. and Trchova, M. (2008). Anticorrosion properties of inorganic pigments surface-modified with a polyaniline phosphate layer. *progress in Organic Coatings,* 63:209–221.

Kamada, K., Tokutomi, M., Enomoto, N. and Hojo, J. (2005).J. Mater. Chem. 15:3388.

Kamaraj, K., Sathiyanarayanan, S., Muthukrishnan, S. and Venkatachari, G. (2009) Corrosion protection of iron by benzoate doped polyaniline containing coatings.Progress in Organic Coatings 64:460–465.

Kang, E. T.; Neoh, K. G. and Tan, K. L. (1998) Polyaniline: a polymer with many interesting intrinsic redox states. *Progress in Polymer Science,* 23: 211-324.

Karlsson. P., Palmqvist. A.E.C., Holmberg. K.(2006).Surface modification for aluminum pigment inhibition. *Advances in Colloid and Interface Science* 128-

130: 121–134.

Kulszewicz-Bajer, I., Zagorska, M., Bany, A. and Kwiatkowski, L.(1999) Polyaniline in doped and undoped form in anti-corrosion coatings. *Synthetic Metals*.102:1385.

Kim, B. J.; Oh, S. G.; Han, M. G. and Im, S. S.(2001) Synthesis and characterization of polyaniline nanoparticles in SDS micellar solutions. *Synthetic Metals*, 122:297–304.

Kim, B. J.; .; Oh, S. G. ; Han, M. G. and Im, S. S.(2000) Preparation of Polyaniline Nanoparticles in Micellar Solutions as Polymerization Medium. *Langmuir*, 16:5841-5845.

Lee, I.S., Lee, J.Y., Sung, J.H. and Choi, H.J. (2005) Synthesis and electrorheological characteristics of polyaniline-titanium dioxide hybrid suspension. Synthetic Metal, 152:173-176.

Lenz, D. M.; Delamar, M. and Ferreira, C. A. (2003). Application of polypyrrole/TiO2 composite films as corrosion protection of mild steel. Journal *of Electroanalytical Chemistry* 540:35– 44.

Li, D. and Kaner , R. B. (2006) Shape and Aggregation Control of Nanoparticles: Not Shaken, Not Stirred. Journal American Chemical Society, 128:968-975.

Li, G. ; Pang, S.; Liu, J.; Wang Z. and Z. Zhang (2006) Synthesis of polyaniline submicrometer-sized tubes with controllable morphology. *Journal of Nanoparticle Research*, 8: 1039–1044.

Li, H., Zhang, Z., Ma, X., Hu, M., Wang, X.Y. and Fan. P. (2007).Synthesis and characterization of epoxy resin modified with nano-SiO_2 and γ glycidoxypropyltrimethoxy silane.*Surface Coating Technology*,201:5269-5272.

Li, X., Wanga, G., Xiaoxuan Lib, Dongming Lu.(2004) Surface properties of polyaniline/nano-TiO_2 composites. *Applied Surface Science*, 229: 395–401.

Li, X., Chen, W., Bian, C., He, J., Xu, N. and Xue, G.(2003) Surface modification of TiO_2 nanoparticles by polyaniline. *Applied Surface Science*, 217:16–22.

Li, X., Wang, D., Luo, Q., An, J., Wang Y. and Cheng G.(2008).Surface modification of titanium dioxide nanoparticles by polyaniline via an *in situ* method. *Journal of Chemical Technology and Biotechnology,* 83:1558–1564.

Li, X., Wang, G., Li, X.(2005) Surface modification of nano-SiO_2 particles using polyaniline. *Surface & Coatings Technology*, 197: 56– 60.

Li, X., Dai, N., Wang, G. and Song, X.(2008) Water-Dispersible Conducting Polyaniline/Nano-SiO_2 Composites without Any Stabilizer. *Journal of Applied Polymer Science,*107: 403–408.

Liu, H.; Kameoka, J. ;Czaplewski, D. A. and Craighead, H. G. (2004) Polymeric Nanowire Chemical Sensor. *NANO LETTERS*, 4: 671-675.

Liu, L. and Levon, K. (1999)Undoped Polyaniline–Surfactant Complex for Corrosion Prevention. *Journal of Applied Polymer Science*.73: 2849–2856.

MacDiarmid, A.(1997) Polyaniline and polypyrrole: Where are we headed?.*Synthetic Metals, 84:*27-34.

Moraes, S. R., Huerta-Vilca, D. and Motheo, A. J. (2003). Corrosion protection of stainless steel by polyaniline electrosynthesized from phosphate buffer solutions. *Progress in Organic Coatings* 48: 28–33.

Neoh, K.G., Tan, K.K., Goh, P.L., Huang, S.W., Kang, E.T. and Tan, K.L.(1999) Electroactive polymer–SiO_2 nanocomposites for metal uptake. Polymer 40: 887-893.

Ngyen, T.D., Ngyen, T.A., Pham, M.C. , Piro, B., Normand, B. and Takenouti, H.(2004) Mechanism for protection of iron corrosion by an intrinsically electronic conducting polymer**.** *Journal of Electroanalytical Chemistry.* 572:225–234.

Niemann.J. (1992). Water bome coatings for the automotive industry. *Progress in Organic Coatings* 21:189-203.

Ogurtsov , N.A. ,. Pud , A.A, Kamarchik , P. and Shapoval, G.S. (2004). Corrosion inhibition of aluminum alloy in chloride mediums by undoped and doped forms of polyaniline . *Synthetic Metals* 143:43–47.

Ogurtsov , N.A., Pud, A.A. , Kamarchik, P. and Shapoval, G.S.(2004) Corrosion inhibition of aluminum alloy in chloride mediums by undoped and doped forms of polyaniline. Synthetic Metals 143: 43–47.

Olad, A. and Rashidzadeh, A.(2008). Preparation and anticorrosive properties of PANI/Na-MMT and PANI/O-MMT nanocomposites. *Progress in Organic Coatings*.62:293–298.

Özyılmaz , A.T., Erbil, M. and Yazıcı, B.(2006a).The electrochemical synthesis of polyaniline on stainless steel and its corrosion performance. *Current Applied Physics* 6: 1–9.

Özyılmaz, A. T. (2005a). The corrosion behavior of polyaniline top coat on nickel plated copper from neutral aqueous medium. *Progress in Organic Coatings* 54:127–133.

Özyılmaz, A. T. (2006b). The corrosion performance of polyaniline film modified on nickel plated copper in aqueous *p*-toluenesulfonic acid solution.*Surface & Coatings Technology* 200: 3918–3925.

Özyılmaz, A. T., Kardaş, G., Erbil, M. and Yazıcı, B. (2005b).The corrosion performance of polyaniline on nickel plated mild steel, *Applied Surface Science* 242: 97–106.

Özyılmaz, A. T., Tűken, T. , Yazıcı, B. and Erbil, M. (2005c).The electrochemical synthesis and corrosion performance of polyaniline on copper. *Progress in Organic Coatings* 52: 92–97.

Özyılmaz, A.T., Erbil, M. and Yazıcı, B.(2006c). The corrosion behaviours of polyaniline coated stainless steel in acidic solutions, *Thin Solid Films* 496: 431–437.

Palaniappan, S. and Amarnath C.A. (2005). Polyaniline-dodecylhydrogensulfate-acid salt: synthesis and characterization. Materials Chemistry and Physics 92:82-88.

Patil, R.C. and Radhakrishnan, S. (2006).Conducting polymer based hybrid nano-composites for enhanced corrosion protective coatings. *Progress in Organic Coatings*.57:332–336.

Popović, M. M. and Grgur, B. N. (2004). Electrochemical synthesis and corrosion behavior of thin polyaniline-benzoate film on mild steel. *Synthetic Metals*143:191–195.

Popović, M.M. , Grgur , B.N. and Misković–Stanković , V.B.(2005).Corrosion studies on electrochemically deposited PANI and PANI/epoxy coatings on mild steel in acid sulfate solution. *Progress in Organic Coatings* 52: 359–365.

Pu, H.T., Qiao, L., Liu, Q.Z. and Yang, Z.L. (2005) a new anhydrous proton conducting material based on phosphoric acid doped polyimide. *European Polymer Journal*.41:2505-2510.

Qi .X. Vetter, C.; Harper .A. C. and Gelling. V. J. (2008). Electrochemical investigations into polypyrrole/aluminum flake pigmented coatings. *Progress in Organic Coatings* 63: 345–351.

Radhakrishnan,S., Siju, C.R., Mahanta,D., Patil,S.,and Madras,G.(2009). Conducting polyaniline–nano-TiO2 composites for smart corrosion resistant coatings. *Electrochimica Acta* 54:1249–1254.

Ray,S.S.(2002) synthesis and evaluation of conductive PolyPyrrole/Al_2O_3 in aqueous and non-aqueous medium. *Material research bulletin* 37:813-824.

Samui, A.B. and Phadnis, S. M. (2005). Polyaniline–dioctyl phosphate salt for corrosion protection of iron. *Progress in Organic Coatings* 54:263–267.

Samui, A.B., Patankar, A.S., Rangarajan, J. and Deb, P.C. (2003).Study of polyaniline containing paint for corrosion prevention. *Progress in Organic Coatings* 47:1–7.

Sapurina , I. ; Riede, A. and Stejskal, J.(2001) in situ-polymerized polyaniline films 3.film formation.*Synthetic metals*, 123; 503-507.

Sathiyanarayanan, S. , Muthukrishnan, S. , Venkatachari, G. and D.C. Trivedi.(2005)

Corrosion protection of steel by polyaniline (PANI) pigmented paint coating, Progress in Organic Coatings 53:297–301.

Sathiyanarayanan, S., Azim, S.S. and Venkatachari G. (2008). Performance Studies of Phosphate-Doped Polyaniline Containing Paint Coating for Corrosion Protection of Aluminium Alloy. *Journal of Applied Polymer Science*:107: 2224–2230.

Sathiyanarayanan, S., Azim, S and Venkatachari, G.(2007a) Preparation of polyaniline–Fe_2O_3 compositeand its anticorrosion performance. *Synthetic Metals* 157:751–757.

Sathiyanarayanan, S., Devi, S. and G. Venkatachari.(2006d) Corrosion protection of stainless steel by electropolymerised PANI coating. *Progress in Organic Coating* 56:114–119.

Sathiyanarayanan, S., Muthukrishnan, S. and Venkatachar, G. (2006a).Performance of polyaniline pigmented vinyl acrylic coating on steel in aqueous solutions. *Progress in organic coating* 55:5–10.

Sathiyanarayanan, S., Muthukrishnan, S. and Venkatachari, G. (2006b) Corrosion protection of steel by polyaniline blended coating. *Electrochimica Acta*51:6313–6319.

Sathiyanarayanan, S., Muthukrishnan, S. and Venkatachari, G. (2006e).Synthesis and anticorrosion properties of polydiphenylamine blended vinyl coatings. *Synthetic Metals*156:1208–1212.

Sathiyanarayanan, S.; Azim, S. S. and Venkatachari, G. (2006c) Corrosion resistant properties of polyaniline–acrylic coating on magnesium alloy, *Applied Surface Science* 253:2113–2117.

Sathiyanarayanan, S., Azim,S. S. and Venkatachari ,G. (2007c) .A new corrosion protection coating with polyaniline–TiO_2 composite for steel, *Electrochimica Acta*,52:2068–2074.

Sathiyanarayanan, S., Azim, S. S. and Venkatachari ,G. (2007d) .Preparation of polyaniline–TiO_2 composite and its comparative corrosion protection performance with polyaniline. *Synthetic Metals*157:205–213.

Sathiyanarayanan, S., Azim, S.S. and Venkatachari , G. (2007e).corrosion protection of magnesium ZM 21 alloy with polyaniline–TiO_2 composite containing coatings. *Progress in Organic Coatings*,59: 291–296.

Sathiyanarayanan,S., Azim, S. S. and Venkatachari, G.(2007b) .Corrosion protection coating containing polyaniline glass flake composite for steel. *Electrochimica Acta* 53:2087–2094.

Schauer, T., Joos, A., Dulog, L., Eisenbach,C.D. (1998). Protection of iron against corrosion with polyaniline primers, *Progress in organic coating* 33: 20–27.

Shacklette, L.W.(1994) Dipole and hydrogen-bonding interactions in polyaniline: a mechanismfor conductivity enhancement. Synthetic metals.**65**:123-130.

Shen, Y. and Wan, M. (1999) Tubular Polypyrrole Synthesized by in Situ Doping Polymerization in the Presence of Organic Function Acids as Dopants. Journal of Polymer Science: Part A: Polymer Chemistry, 37:1443–1449.

Shi, H., Liu, F., Yang, L and Han,E. (2008). Characterization of protective performance of epoxy reinforced with nanometer-sized TiO_2 and SiO_2. *Progress in Organic Coatings,* 62: 359–368.

Solange de Souza. (2007) .Smart coating based on polyaniline acrylic blend for corrosion protection of different metals. *Surface & Coatings Technology,* 201:7574–7581.

Stejskal, J., Heavata, D., Hollar, P., Trchora, M., Prokes, J. and Sapurina,I.(2004) *Polymer International*.53:294–300.

Su, W. and Iroh, J.O. (2000).*Journal of Adhesion Science* 73: 215-231.

Su, W. and Iroh, J.O. (2000). Electrodeposition mechanism, adhesion and corrosion performance of polypyrrole and poly(*N*-methylpyrrole) coatings on steel substrates. *Synthetic Metals* 114: 225–234.

Su, S. J. and Kuramuto, N. (2000) Processable Polyaniline–titanium dioxide nanocomposites: effect of titanium dioxide on the conductivity.*Synthetic*

Metal 114: 147-153.

Sung. L., Nadal. M. E., McKnight. M. E., Marx.E. and Dutruc. R.(2001).Effect of aluminum flack orientation on coating appearance. *National Institute of Standards and Technology*,Gaithersburg. MD 20899-8621 USA.

Tallman .D. E., Levine .K. L., Siripirom .C. , Gelling .V. G., Bierwagen .G. P., Croll, S. G. (2008). Nanocomposite of polypyrrole and alumina nanoparticles as a coating filler for the corrosion protection of aluminium alloy 2024-T3. *Applied Surface Science,* 254: 5452–5459.

Tansuğ, G., Tüken,T., özyılmaz, A.T., Erbil, M.and Yazıcı, B.(2007). Mild steel protection with epoxy top coated polypyrrole and polyaniline in 3.5% NaCl. *Current Applied Physics,* 7: 440–445.

Tang, S.; Jing, X.B.; Wang, B.C. and Wang, F. (1988). Infrared spectra of soluble polyaniline, *Synthetic Metals, 24:* 231 – 238.

Tarachiwin, L., Kiattibutr, P., Ruangchuay, L., Sirivat, A., Schwank, J. (2002) Electrical conductivity response of polyaniline films to ethanol-water mixtures. *Synthetic Metal.*129: 303-308.

Teoh, G.L., Liew, K.Y.,. Mahmood, W.A.K.(2007). Preparation of polyaniline-Al_2O_3 composites nanofibers with controllable conductivity. *Materials Letters* 61: 4947–4949.

Terje A. Skotheim and John R. Reynolds.(2007) Conducting Polymers (3th Ed.) U.S.6000 Broken Sound Parkway NW. CRC Press Taylor & Francis Group.

Tüken, T. (2006a).Zinc deposited polymer coatings for copper protection. *Progress in Organic Coatings* 55:60–65.

Tüken, T., Özyilmaz, A.T. , Yazici, B., Kardaş¸ G.and Erbil, M.(2004) Polypyrrole and polyaniline top coats on nickel coated mild steel, *Progress in Organic Coatings* 51 : 27–35.

Tüken, T., Yazıcı, B. and Erbil, M.(2006b).Zinc modified polyaniline coating for mild steel protection. *Materials Chemistry and Physics* 99: 459–464.

Virji, S. ; Huang, J. ; Kaner , R. B. and Weiller , B. H. (2004) Polyaniline Nanofiber Gas Sensors: Examination of Response Mechanisms. *NANO LETTERS*, 4: 491-496.

Wan, M. (1989) The influence of polymerization method and temperature on the absorption spectra and morphology of polyaniline. *Synthetic Metals,31:*51-59.

Wang, L.,Wang,K., Chen, L., Zhang, Y. and He. C. (2006). Preparation, morphology and thermal/mechanical properties of epoxy/nanoclay composite.Composites: Part A, 37: 1890–1896.

Wei, Z. ; Zhang, Z. and Wan, M.(2002) Formation Mechanism of Self-Assembled Polyaniline Micro/Nanotubes . *Langmuir,* 18: 917-921.

Wei, Z. *and Wan, M.* (2002) hollow micro spheres of polyaniline synthesized with an aniline emulsion template.*Advanced Materials,* 14:1314-317.

Xia, H., Narayanan, J., Cheng, D., Xiao, C. Liu, X. and Chan, H. S. O. (2005). Formation of Ordered Arrays of Oriented Polyaniline Nanoparticle Nanorods. *J. Phys. Chem. B,109:* 12677-12684.

Xu, J., Liu, W. and Li, H.(2005) Titanium dioxide doped polyaniline. *Materials Science and Engineering C,* 25: 444-447.

Yang, Q-L ; Zahia, J ; Feng,L ; Song,Y-L; Wan,M-X; Jiang ,L; Xu, W-G and Li, Q-S. (2003).Synthesis and characterization of conducting polyaniline/γ-Fe2O3 magnetic nanocomposite. Synthetic Metals, 135–136: 819–820

Yano, S., Ito,T., Shinoda,K., Ikake,H., Hagiwara,T., Sawaguchi,T., Kurita,K. and Seno,M. (2005). Properties and microstructures of epoxy resin/TiO_2 and SiO_2 hybrids. *Polymer International*,54:354–361.

Yao, X.F., Zhou, D .and Yeh, H.Y. (2008) Macro/microscopic fracture characterizations of SiO2/epoxy nanocomposites. *Aerospace Science and Technology*,12:223–230.

Yao, X.F., Zhou, D.and Yeh, H.Y.(2005). Macro/microscopic fracture characterizations of SiO_2/epoxy nanocomposites. *Aerospace Science and*

Technology, 12: 223–230.

Yeh, J.M., Liou, S.J., Lai, C.Y. and Wu, P.C. (2001). Enhancement of Corrosion Protection Effect in Polyaniline via the Formation of Polyaniline-Clay Nanocomposite Materials. *Chem.Mater*,13:1131-1136.

Yoon, C. O., Kim, J. H., Sung, H. K. and Lee, H. (1997) Electrical conductivity and thermopower of phosphoric acid doped polyaniline. *Synthetic Metals*.84:789-790.

Yoon S. Lee. (2008).self-Assembly and nanotechnology. Canada : John Wiley & Sons.

Zarras, P., Anderson, N., Webber, C., Irvin, D.J., Irvin, J.A., Guenthner, A.and Stenger-Smith, J.D. (2003). Progress in using conductive polymers as corrosion-inhibiting coatings. *Radiation Physics and Chemistry,* 68: 387–394.

Zhai, L., Ling, G.P. and Wang, Y.W. (2007) Effect of nano-Al_2O_3 on adhesion strength of epoxy adhesive and steel. *International Journal of Adhesion & Adhesives,* 28: 23–28.

Zhai. L.L., Ling. G.P., Li. J and Wang. Y.W (2006). The effect of nano particles on the adhesion of epoxy adhesive, *Materials Letters*, 60:3031–3033.

Zhang , L. ; Zhang , L. and Wan, M. (2008) Molybdic acid doped polyaniline micro/nanostructures via a self-assembly process. European Polymer Journal 44:2040–2045.

Zhang , X., Wang ,F. and Du, Y.(2007) Effect of nano-sized titanium powder addition on corrosion performance of epoxy coatings. *Surface & Coatings Technology*,201: 7241–7245.

Zhang , Z. ; Wei , Z. ; Zhang , L. and Wan, M.(2005) Polyaniline nanotubes and their dendrites doped with different naphthalene sulfonic acids. Acta Materialia, 53:1373-1379.

Zhang, D. (2006). Preparation of Core–Shell Structured Alumina–Polyaniline Particles and Their Application for Corrosion Protection. *Applied Polymer*

Science,101:4372–4377.

Zhang, J.; Ge, Z.; Jiang, X.; Hassan, P.A. and Liu, S. (2007) Stopped-flow kinetic studies of sphere-to-rod transitions of sodium alkyl sulfate micelles induced by hydrotropic salt. *Journal of Colloid and Interface Science*, 316:796–802.

Zhang, X., Xu, W., Xia, X., Zhang, Z. and Yu ,R.(2006) Toughening of cycloaliphatic epoxy resin by nanosize silicon dioxide. *Materials Letters*, 60:3319–3323.

Zhang, Z. ; Wei, Z. and Wan, M. (2002) Nanostructures of Polyaniline Doped with Inorganic Acids. *Macromolecules*, 35:5937-5942.

Zhao. H. and Li. R. K.Y. (2008). Effect of water absorption on the mechanical and dielectric properties of nano-alumina filled epoxy nanocomposites. *Composites:Part A*, 39: 602–611.

Zubillaga , O. , Cano , F.J. , Azkarate , I., Molchan , I.S. , Thompson , G.E. , Cabral A.M. and Morais , P.J.(2008).Corrosion performance of anodic filmsccontaining polyaniline and TiO_2 nanoparticles on AA3105 aluminium alloy.