THE EFFECTS OF CARBON BLACK IN EPOXY COATING FILLED POLYANILINE/NANO-ZINC/CARBON BLACK ON CORROSION RESISTANCE

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To my parents
for their love, endless support
and encouragement.

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ABSTRACT

The main objective of this research is to study the effects of polyaniline (PAni)/nano-zinc/carbon black/epoxy coating on the corrosion resistance of carbon steel substrate. The anticorrosion coating material was prepared by mixing the PAni, nano-zinc powder, carbon black and epoxy resin. The PAni content and nano-zinc powder content were fixed at 0.3 wt% and 1wt% while the carbon black contents were varied from 0, 0.5, 1 and 1.5 wt%. The PAni was synthesized via chemical method and characterized by Fourier Transformed Infrared (FTIR). The corrosion resistance of PAni/nano-zinc/carbon black/epoxy coated substrate was evaluated using immersion test and the interaction between the four components of coated material was analyzed by FTIR. Thermogravimetric analysis (TGA) is used to evaluate the thermal stability of the PAni/nano-zinc/carbon black/epoxy coating materials. Analysis of the absorption peaks in FTIR spectrum of synthesized PAni-ES has confirmed that the produced green powder was PAni. Conductivity test proved an acceptable conductivity of 0.6-0.9 S/cm. From the results, it was found that epoxy coating with PAni alone and nano-zinc powder alone have reduced the corrosion rate of epoxy coating. The combination of PAni and nano-zinc powder had further reduced the corrosion rate of coating materials. The PAni/nano-zinc/carbon black/epoxy coating material have increase the corrosion resistance of carbon steel substrate and the protection of corrosion is further increased with increasing of carbon black powder contents. FTIR analysis of final coating materials showed very similar absorption peaks in seven different coating compositions which proved that there is no chemical bonding to make shifting in peaks in comparison between different formulations. From TGA results, the onset degradation temperature increased with the incorporation of PAni, nano-zinc and carbon black.

ABSTRAK

Objektif utama penyelidikan ini adalah untuk mengkaji kesan bahan salutan epoksi/polianilin (PAni)/zink-nano/karbon hitam ke atas rintangan karatan pada substrate keluli karbon. Bahan salutan anti karat telah disediakan dengan mencampurkan resin epoksi, polianilin (PAni), karbon hitam dan serbuk zink-nano. Kandungan PAni dan serbuk zink-nano telah ditetapkan pada 0.3% dan 1 wt% sementara kandungan karbon hitam berubah-ubah dari 0, 0.5, 1 dan 1.5 wt%. PAni telah disintesiskan melalui kaedah kimia dan dicirikan menggunakan spektroskopi infra merah (FTIR). Ketahanan terhadap karatan, substrate yang bersalut epoksi/polianilin/zink-nano/karbon hitam telah diuji menggunakan ujian rendaman dan interaksi diantara empat komponen bahan salutan tersebut telah dianalisa menggunakan FTIR. Analisis gravimetric terma (TGA) digunakan untuk menilai kestabilan terma bahan salutan epoksi/polianilin/zink-nano/karbon hitam. Analisa FTIR spektrum untuk PAni-ES yang disintesis telah mengesahkan bahawa serbuk hijau yang dihasilkan adalah PAni. Ujian konduktiviti membuktikan nilai konduktiviti yang boleh diterima pakai diantara 0.6-0.9 S/cm diperolehi. Daripada keputusan yang diperolehi, didapati salutan epoksi yang mengandungi PAni sahaja dan serbuk zink-nano sahaja telah mengurangkan kadar karatan salutan epoksi. Gabungan PAni dan serbuk zink-nano di dalam salutan epoksi telah mengurangkan lagi kadar karatan bahan salutan tersebut. Bahan salutan epoksi/polianilin/zink-nano/karbon hitam telah meningkatkan rintangan terhadap karatan substrate keluli karbon dan perlindungan terhadap karatan semakin tinggi dengan peningkatan kandungan serbuk karbon hitam. Analisa FTIR untuk bahan salutan akhir menunjukkan puncak serapan yang sangat sama untuk ketujuh-tujuh komposisi bahan salutan yang berbeza dimana ianya membuktikan bahawa tiada ikatan kimia berlaku untuk merubah puncak serapan tersebut. Daripada keputusan TGA, suhu degradasi onset meningkat dengan penambahan PAni, zink-nano dan karbon hitam.

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LIST OF ABBREVIATIONS/SYMBOLS

PAni	-	Polyaniline
APS	-	Ammonium pereoxdisulfate
$C_6H_5NH_2$	-	Aniline
CNT	-	Carbon Nanotubes
CB	-	Carbon Black
ICPS	-	Inherently Conductive Polymer
Na	-	Sodium
K	-	Potassium
Li	-	Lithium
PAni-ES	-	polyaniline Emeraldine Salt
PAni-EB	-	polyaniline Emeraldine base
OH	-	Hydroxyl ions
Fe^{+2}	-	Ferrous ions
BPF	-	Bisphenol F
BPA	-	Bisphenol A
EPN	-	Epoxy Phenol novolacs
NaCl	-	Sodium chloride
EIS	-	Electrochemical Impedance Spectroscopy
VOC	-	Volatile Organic Compounds
HCl	-	Hydrochloric Acid
$C_6H_4(CH_3)_2$	-	Xylene
C_4H_9OH	-	1-Butanol
TGA	-	Thermogravimetric analysis

K	-	A constant
A	-	Area
t	-	Time
ρ	-	Density
W	-	Mass loss in g, to nearest 1 mg

CHAPTER 1

INTRODUCTION

1.1 Background of the Problem

Epoxy coating has been widely use as a protection layer for steel in concrete structures, due to its good processability, electrical insulating properties, good performance in chemical resistance and strong adhesion to heterogeneous materials. They are two ways that epoxy coatings react to decrease the corrosion of a metal substrate which was subjected to an electrolyte; 1) become a physical barrier layer to control the attack from deleterious species and 2) serve as a source for corrosion inhibitors to protect the steel surface in resisting attack by species such as chloride anions (Radhakrishnan et al.,2009; Shi et al.,2009).

Electrically conductive polymers are new class of polymers which are capable of acting as anti-corrosion materials. The development of the processibility of conductive polymer has facilitated the increase performance of practical applications. PAni has been established to be very effective material for corrosion protection (Talo *et al.* 1997). In addition, the corrosion resistance of PAni Coatings seem to expand to scratched areas where a metal surface is exposed to an aggressive environment. It is proven by two standards testing which are corrosion testing and electrochemical plus surface analytical methods (Lu et al., 1995).

PAni is an important constituent for corrosion protection in coatings materials. PAni based coatings materials can protect the steel surface from corrosion. The PAni based coatings can be prepared either from directly deposited PAni on metal surface by electrochemical method or chemically synthesized PAni (Radhakrishnan et al., 2009).

Zinc-rich coatings are effective in protecting steel against corrosion. The principle of this protective action is attributed to the fact that zinc, being higher than iron in the electromotive series of the elements reacts first in any environment conductive to the ionic dissolution (oxidation) of metals, thereby protecting the steel substrate. As the name implies, zinc-rich coatings contain a high concentration of zinc in the dry film. This is required so as to provide the electrical continuity and, therefore, the conductivity necessary for the electrochemical process to take place. In order to obtain these zinc-rich coatings on a ferrous substrate, a paint formulation containing very fine zinc dust produced by distilling the metal under controlled conditions of condensation is used. When the paint is applied, the metallic powder is held in place on the surface by a binder matrix. Zinc-rich coatings are classified, according to the nature of the binder, into organic or inorganic coatings. Organic zinc-rich coatings utilize synthetic polymers as binders. Although such coatings afford effective corrosion protection, their heat and solvent resistance are limited. Inorganic binders do not have these limitations.

Previously macro size zinc dust with volume of between 700 to 900 gm/kg in epoxy resin was used to protect the metal surface (Shreepathia *et al*., 2008; Marchebois *et al*., 2002). The micron size of zinc powders with this content in the coating is the best average range of the powder for cathodic protection (Shreepathia *et al*., 2008). As it is known, the nano size powders provide bigger contact surface area compared to macro size powder thus the amount needed in the coating material is reduced (Hakima *et al*., 2007). The properties will be enhanced by using a small amount of nano size powders (Marchebois *et al*., 2002). Most of the times the properties such as mechanical, barrier, corrosion and thermal properties of nano size powders are better than macro sized powders.

One technique to improve the adhesion and anti corrosive properties of polymer is by the addition of nano-particles. Silicates and carbon nanotubes (CNT) are the most common nano-particles used either to creating specific functionalized properties or as reinforcement's materials. The nano-particles have been modified to have different functionalities to get different properties such as increase the electrical conductivity, thermal conductivity, proton conductivity of materials and cohesion properties of films and strengthening of adhesion. Cohesion properties reflect the strength and fracture resistance of the materials, while adhesion properties reflect the interfacial bond strength of coatings or adhesives (Aglan et al., 2007).

The second phases which are miscible in the epoxy are used to improve the barrier performance of epoxy coatings by zigzagging the diffusion path for deleterious species and decreasing the porosity. A nano scale inorganic filler particles can be dispersed and distributed inside the epoxy resin to produce an epoxy nano composite. The advantages of using nano-particles are to increase the durability, integrity of coatings and at the same time it is environmental friendly. This is due to the fact that, nano-particles dispersed in coatings can fill up the cavities and cause a reduction in crack propagation. Nano-particles can also prevent epoxy separation when curing thus giving more homogenous coating materials. Epoxy coatings containing nano-particles give a good barrier properties for protection from corrosion and limits the coating to delaminate or blister (Shi et al., 2009).

Carbon black is widely used in application such as black pigment, inks and as a conductive agent in advance material. It consists of fine carbon particles. Various features of carbon black are controlled in production by partially combusting oil or gases (http://www.carbonblack.jp/en/cb/youto.html).

Currently many works have concentrate on the use of hybrid filler. The combination effects from nano-particle filler and conductive polymer have increased the corrosion protection of metal sample (Shi *et al*., 2009; Pavlidou et al2008; Zaki, 2006).

1.2 Problem Statement

The corrosion is one of the most crucial issues which mankind has been faced. Corrosion naturally impacts our daily life through chemical reactions that occur between metals or metal alloys and their environment because metals turn 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 PAni 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 pigments are distributed in each and everywhere in organic coating (Sathiyanarayanana, 2006).

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 many years zinc-rich primer has been used as the corrosion protection layer in coating systems. The effect of nano-zinc powder in epoxy resin binder has been studied by Shi *et al*. (2009) and found that epoxy coatings containing nano-particles offer significant barrier properties for corrosion protection and reduce the trend for the coating to blister or delaminate.

In order to enhance the corrosion protection, many works have concentrated on the use of hybrid filler in coating material. Nima Moezani (2011) reported that, 1 and 1.5 phr nano-zinc content in epoxy/ polypyrrole coating had produced the best coating formulation for corrosion protection of carbon steel.

The mixtures of PAni, nano-zinc dust and carbon black in powder form as corrosion inhibitor for extra protection on metal surface has never been evaluated. In this study the corrosion resistance and thermal stability of hybrid epoxy coating have been studied.

1.3 Objective of the Study

The objective of this research is to assess corrosion resistance of epoxy coating resin filled with PAni conductive polymer, nano-zinc and carbon black:

1- To investigate the degree of corrosion resistance of epoxy coating containing hybrid filler (PAni/ nano-zinc/ carbon black) via immersion test.

2- To determine the interaction of PAni, nano-zinc, carbon black and epoxy in coating materials via FTIR analysis.

3- To determine the effect of different carbon black content on the thermal stability (TGA) of hybrid epoxy coating.

1.4 Scope of the Study

In order to achieve the objectives, the following factors were investigated:

1- Synthesizing PAni from aniline monomer by using chemical method.

2- Mixing of PAni (0.3 wt %) , nano-zinc (1 wt %) and carbon black (0, 0.5 , 1 , 1.5 wt %) with epoxy resin to prepare four samples of PAni/nano-zinc/carbon black/epoxy paint coating composition.

3- Analyzing of the samples using Thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

4- Applying PAni/nano-zinc/carbon black/epoxy paint coatings composition to carbon steel.

5- Measurement of the coated carbon steel corrosion by using immersion test.

6- Analyzing of the synthesized PAni using Fourier Transform Infrared Spectroscopy (FTIR) and employing conducting test to it.

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