

**A STUDY ON THE CHARACTERISTICS OF COPPER AND
COPPER OXIDE-BASED ANTIFOULING COATINGS**

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**FACULTY OF SCIENCE
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**A STUDY ON THE CHARACTERISTICS OF COPPER AND
COPPER OXIDE-BASED ANTIFOULING COATINGS**

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ABSTRACT

Coating is the easiest and cheapest method to prevent corrosion. Every country spends enormous money due to the adverse effect of corrosion. Marine industry is facing lot of issues because of corrosion and biofouling problems. There are restrictions to use harmful biocides in antifouling coatings for boats, yachts and ships. In the market, antifouling coatings have been developed using more than 50 wt% of biocide loading. In this work, an attempt was made to reduce the usage of biocide to protect the ocean environment and production cost. In this work, polyester-epoxy resins have been used as the binder to formulate the coating system. The developed coating systems were analysed to evaluate physical, mechanical, structural, thermal and electrochemical properties. The anticorrosion property was examined by electrochemical impedance spectroscopy. The variation of coating resistance, R_c was calculated by analyzing the Bode plot from the impedance data obtained. From FTIR and DSC studies, the formation of crosslinking between the resins was explained. From the performance analyses, the binder system consisting of 90 wt% polyester and 10 wt% epoxy has shown better performance compared to other compositions. It has been selected to develop antifouling coatings. Copper and copper oxides were added as biocide in the antifouling coating system. The optimum pigment volume concentrations of the biocides were found. The best coating resistance, R_c for both copper and copper oxide binder system was found to be in the order of 10^8 ohm at the end of 30 days of exposure in artificial seawater. Antifouling property of this developed coatings depend on the leaching of the biocide from the coatings. The leaching has been measured by immersing the coated panels in different electrolyte solutions. The electrolyte samples were tested by ICP-OES. The metal concentration in different types of electrolytes reveals that the amount of leaching is greater for the seawater as compared to the distilled water and artificial seawater. The real-time seawater exposure test was carried

at two locations such as Lumut, Perak and Penang Island in Malaysia. The copper oxide based antifouling coating system showed the best performance in real exposure in seawater since the adhesion of the coating to the steel plates was very good. The microorganism growth on the coated panels was prevented by the leaching of biocide. It has been confirmed by SEM micrographs which were free of microorganism on the surface. From the results it was found that 25 % PVC of copper based antifouling coating and 25 % PVC of copper oxide based antifouling coating showed better performance. Booster biocide (diuron) was added from 1wt. % to 5 wt.% into the two best antifouling coating systems to study the effect of diuron on the antifouling properties. SEM micrographs revealed that the performance of the copper oxide-diuron antifouling coating system was better than the copper oxide antifouling coating system.

ABSTRAK

Salutan adalah kaedah yang paling mudah dan termurah untuk mencegah hakisan. Setiap negara membelanjakan wang yang besar disebabkan oleh kesan daripada hakisan. Industri Marin menghadapi banyak isu-isu yang disebabkan oleh hakisan dan masalah biofouling. Terdapat sekatan untuk menggunakan penyertaan berbahaya dalam lapisan antifouling bot, kapal layar dan kapal-kapal. Di pasaran, lapisan antifouling telah dibangunkan menggunakan memuatkan lebih 50 % berat biocide. Dalam karya ini, usaha telah dibuat untuk mengurangkan penggunaan biocide untuk melindungi kos pengeluaran dan persekitaran laut. Dalam karya ini, poliester-epoxy resin telah digunakan sebagai pengikat dalam merangka sistem salutan. Sistem salutan yang telah dibangunkan dianalisa untuk menilai ciri-ciri fizikal, mekanikal, struktur, haba dan elektrokimia. Ciri-ciri salutan anti karat telah diperiksa oleh spektroskopi impedans elektrokimia. Variasi salutan rintangan, R_c telah dikira dengan menganalisis plot Bode berpandukan data impedans yang diperolehi. Dari kajian FTIR dan DSC, pembentukan crosslinking antara resin-resin diperjelaskan. Dari analisis prestasi, sistem pengikat yang terdiri daripada 90 wt % poliester dan 10 wt % epoksi telah menunjukkan prestasi yang lebih baik berbanding komposisi lain. Ia telah dipilih untuk membangunkan salutan antifouling. Kuprum oksida dan kuprum ditambah sebagai biocide dalam sistem salutan antifouling. Peratusan kepekatan isipadu pigmen biocide yang optimum dapat ditemui. Ketahanan rintangan salutan terbaik, R_c untuk kedua-dua oksida kuprum dan kuprum dalam sistem pengikat yang diperolehi berada dalam perintah itu 10^8 ohm pada hari ke-30 di dalam air laut yang tiruan. Ciri-ciri antifouling salutan ini bergantung kepada kepekatan larut lesap biocide dari lapisan salutan. Kepekatan larut lesap itu diukur dengan merendam panel bersalut dalam elektrolit yang berbeza. Sampel elektrolit telah diuji menggunakan ICP-OES. Keputusan kepekatan logam dalam jenis elektrolit yang berbeza mendedahkan bahawa jumlah larut lesap adalah lebih besar

dalam air laut yang berbanding air suling dan air laut yang tiruan. Ujian pendedahan masa sebenar telah diadakan di dua lokasi seperti di Lumut, Perak dan Pulau Pinang di Malaysia. Sistem salutan antifouling berasaskan kuprum oksida menunjukkan prestasi terbaik dalam pendedahan sebenar dalam air laut apabila lekat kepada panel besi dengan sangat baik. Pertumbuhan mikroorganisma pada panel bersalut dapat dihalang oleh larut lesap biocide. Ia telah disahkan oleh micrographs SEM yang bebas daripada mikroorganisma di permukaan. Dari keputusan didapati bahawa salutan antifouling dengan komposisi 25% kepekatan isipadu berasaskan kuprum dan 25% kepekatan isipadu berasaskan kuprum oksida menunjukkan prestasi yang lebih baik. Biocide penggalak (diuron) telah ditambah dari 1% ke 5 % berat ke dalam sistem salutan antifouling untuk mengkaji kesan diuron pada ciri-ciri salutan antifouling. SEM micrographs mendedahkan bahawa prestasi sistem salutan antifouling kuprum oksida-diuron adalah lebih baik daripada sistem salutan antifouling kuprum oksida.

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LIST OF ABBREVIATIONS

| | |
|----------------|--|
| Cu | Copper |
| CuO | copper oxide |
| PVC | pigment volume concentration |
| CPVC | critical pigment volume concentration |
| NaCl | sodium chloride |
| R _c | coating resistance/coating pore resistance |
| T _g | glass transition temperature |
| EIS | electrical impedance spectroscopy |
| ICP-OES | inductively coupled plasma optical emission spectrometry |
| DSC | differential scanning calorimetry |
| FTIR | fourier transform infrared spectroscopy |
| SEM | scanning electron microscope |

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CHAPTER 1: INTRODUCTION

1.0 Background

Protective coating is one of the methods used to prevent corrosion. It is one of the economical ways to protect metallic substrates against aggressive and corrosive environment. Antifouling paint coatings on ships are used in a wide range of functions such as corrosion resistance, ease of maintenance, appearance, non-slip surfaces on decking as well as the prevention of fouling on the hull by unwanted marine organism (Chambers *et al.*, 2006). Prolonged exposure to seawater usually results in the growth of algae, barnacles and other marine organisms on the hull as well as on other parts of a ship. Such growth can affect the ship's performance since it will reduce speed and can also increase fuel consumption (Bressy and Margailan, 2009; Buma *et al.*, 2009; Dafforn *et al.*, 2011).

Generally, antifouling coatings comprise of binders and biocides in polymer matrixes. A paint/coating system may also be formulated by the combination of binder, pigment, extenders and additives such as dryers, hardening agents, stabilizing agents, surface activating compounds, and dispersion agents. The formulation of coating systems using different resins can be achieved by interaction of these polymer molecules using curing agents. Acrylic, epoxy, polyester and silicone resins can be used for the formulation of a paint system. These resins have good adhesion, impact resistance, thermal resistance and corrosion resistance (Kumar and Sasikumar, 2010; Bressy and Margailan, 2009; Fay *et al.*, 2007).

Initially, tributyltin (TBT) was introduced as biocides in marine antifouling coatings and has been used to kill microorganisms on the coating surface and prevent biofouling (Dafforn *et al.*, 2011). Unfortunately, the use of TBT was banned by International Marine Organization (IMO) due to the harmful effect to the marine environment (Marcheselli *et al.*, 2011; Dafforn *et al.*, 2011; Kumar and Sasikumar, 2010). In the past decade, several tin-free products have reached the commercial market, and claimed their effectiveness as regards to the prevention of marine biofouling on ships in an environmentally friendly manner (Dafforn *et al.*, 2011; IMO, 2001; Yebra *et al.*, 2004). As an alternative, biocides with reduced toxicity were developed (Buma *et al.*, 2009). Copper and zinc has been widely used in one of the antifouling paints (Singh and Turner, 2009).

Copper has been used for a long time as biocide in a coating system. The biocides acts like pesticides. The leaching and diffusion of the biocides from the paint surface will prevent the microorganism to adhere on the surface of the coating material. The performance of the antifouling coatings depends on the diffusion mechanism in the performance of the biocides. The leaching rates of the biocides must be controlled in order to slow down the reaction with seawater and other seawater ions within the paint pores (Yebra *et al.*, 2004). If the leaching is not controlled, the seawater condition can be affected giving negative impact to the seawater population. The contemporary antifouling formulation has used more copper as active pigments which inhibit the settlement of the marine organism (Singh and Turner, 2009). In the self-polishing coatings, the leaching rate is higher and hence, the replacement of new coatings will have to be done frequently. The available antifouling coatings have used more and more copper in the composition resulting in expensive paint materials.

Copper pyrothione, zinc pyrothione, diuron, irgarol and other biocides can be considered for use as booster biocides (Buma *et al.*, 2009). These biocides are used as bactericides, fungicides and algacides since they have a broad spectrum of antimicrobial activity against most of the microorganisms. Toxicity due to the release of these compounds into the environment is very low and will not affect fish and other sea creatures (Dafforn *et al.*, 2011; Turley *et al.*, 2000). The objective of this study is to use these additional non-toxic booster biocides along with copper to reduce the cost and increase the antifouling ability.

Since the fifties, researchers have put in a lot of effort to develop effective antifouling coatings that can improve coating/paint systems available in the market. The focus is more on the prevention of marine biofouling on ships in an environmental friendly manner. The antifouling characteristics of a coating system can be determined by a few antifouling properties such as the effect of corrosion, adhesion of coating to the substrate, surface smoothness/glossiness, durability, color and other related physical properties. An in depth explanation of the antifouling characteristics and properties studied by other researchers are discussed in chapter two.

1.1 Objectives

In this work, four antifouling coating systems have been studied. These systems are the epoxy-polyester binder system, copper biocide system, copper oxide biocide system and copper oxide-diuron coating system. It is our intention to use the blended polymer resin binder (polyester and epoxy) as it will enhance the antifouling and anticorrosion properties of a coating system. To the knowledge of the author, there is no literature that has reported on the incorporation of such biocides with this type of binder. Copper and copper oxide was chosen as the biocides to prevent the adhesion of micro and macroorganisms on the coated panels and to increase the coating resistance

performance. The optimum performance for the coating system has been added with the booster biocides; in this case we use diuron to enhance the coating resistance and adhesion performance. Diuron is known as a type of booster biocides that has been used in antifouling coating system which can help to reduce toxicity levels in seawater (Buma *et al.*, 2009). It is also a non-ionic with moderate water soluble compound that works to reduce the germination and growth of non target algae, exhibits low degradation and as photosynthesis inhibitor (Dafforn *et al.*, 2011; Yebra *et al.*, 2004).

The binder coated system has been characterised using differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR) and pull of adhesion test to study the thermal, structural bonding and mechanical properties of the polyester-epoxy binder system. Meanwhile, the selected biocides coated panels have been characterized using electrical impedance spectroscopy (EIS), scanning electron microscopy (SEM), inductively coupled plasma-optical emission spectroscopy (ICP-OES), glossiness test and the physical studies with real exposure in seawater environment.

The aims of this work are listed as follows:

- a) To develop the copper and copper oxide based antifouling coatings with polyester/epoxy binders.
- b) To determine the composition of biocides which will gives the highest performance of the coating resistance at room temperature. The anticorrosion effect has been studied in terms of the coating resistance. For good anticorrosion effect the coating resistance should be high.
- c) To characterize the coating systems prepared on mild steel panels using EIS, ICP-OES, SEM, gloss meter with respect to exposure in seawater for 30 days.

For the lab test, the coating resistance can be determined using electrical impedance spectroscopy (EIS) by analyzing the Bode plot constructed from the impedance data. The leaching mechanism of the coated panels can be studied via ICP-OES test to determine the metal leaching concentration of the copper/copper based coating systems. The metal (biocides) concentration has been obtained within 30 days of immersion with different types of electrolytes.

1.2 Scope of Study

This thesis consists of ten chapters. In this work, the blended polyester and epoxy resin have been analyzed to determine the best coating performance of the binder coating system. The effect of addition of biocides and booster biocides with the hybrid polymer resin were then characterized to study the antifouling properties of the prepared coating system.

Some overview on coating/paint systems is described in Chapter Two. Chapter Three describes the methods of sample preparation and the techniques used to characterize of the coating systems prepared.

Results on coating resistance with different types of biocides are described in Chapter Four for the all coating systems. The leaching rates of the copper and copper oxide from the coated panels were determined to study the leaching mechanism of the biocides in different types of electrolyte. It is well known that the biocides can prevent the microorganism growth on the coated surface. In order to determine the metal concentration, ICP-OES lab test was performed and the results presented in Chapter Five.

The real exposure in seawater environment was carried out in two locations at Lumut, Perak and Penang Island, Malaysia to study the effect of the seawater exposure

to the prepared antifouling coating systems. The coated panels were immersed in the seawater for 30 continuous days to see the physical effects on the coated surface. The pictures were taken every 10 days of intervals and the physical effects were recorded. The physical effects were presented in Chapter Six.

The glossiness of the coated panels was then analyzed to study the difference before and after exposure in seawater. The results are presented in Chapter Seven. The morphology of the coated panels was then obtained from SEM to see the surface changes effects. The results are discussed in Chapter Eight.

An in depth discussion is presented in Chapter Nine and the thesis ends with the proper conclusions and suggestions that are dealt in Chapter Ten.

University of Malaysia

CHAPTER 2: LITERATURE REVIEW

2.0 Introduction

For a number of years, coatings have been the most convenient method of corrosion prevention and fouling protection of steel surfaces, ship bottoms and their structures, storage tanks and surface of the pipelines (Yebra *et al.*, 2004). Numerous coating systems based on epoxy and unsaturated polyester (UP) resins are available for industrial and submerged structures, but they are not completely satisfactory from the viewpoint of corrosion prevention and fouling protection (Anand Prabu and Alagar, 2004).

The continuous contact with seawater of ships and boats has led to the formation and growth of microorganisms such as algae and barnacles (Buma *et al.*, 2009; Dafforn *et al.*, 2011). Figure 2.1 shows the example of microorganism growth on a ship hull (Yebra *et al.*, 2004).



Figure 2.1: Example of the heavily fouled hull (Yebra *et al.*, 2004)

The biocide materials such as tin, zinc, copper has been previously used as the antifouling coating material (Marcheselli *et al.*, 2011; Yebra *et al.*, 2004). The antifouling paint mixture that has been widely used is the epoxy resin based with metal or other metal oxide. However, the use of copper metal in the antifouling paints has led to the high cost for the maintenance of the ship hull.

The polymer resins such as acrylic, epoxy, polyester and silicone resins can be used for the formulation of paint systems (Kumar and Sasikumar, 2010). Most of the available antifouling paints have used epoxy resin and acrylic resins separately. The antifouling and anticorrosion properties can be enhanced by combining of these resins to form a cross linking network hybrid polymer resin (Kumar and Sasikumar, 2010; Prabu and Alagar, 2004).

Booster biocides such as copper pyrothione, zinc pyrothione (Buma *et al.*, 2009), econea and other biocides can be used to enhance the performance of the binder system. These biocides are used to enhance the antifouling ability on the hull's surface. In many cases, the use of toxic antifouling paints has been the main choice in marine applications (Ananda Kumar and Sasikumar, 2010). The use of the booster biocides (copper pyrothione and zinc pyrothione) can be used as an ideal replacement for TBT in marine antifouling paints (Turley *et al.*, 2000). These compounds are low in toxicity and will not affect the marine population such as fish and other sea creatures (Dafforn *et al.*, 2011, Turley *et al.*, 2000).

2.1 Coatings/Paints

2.1.1 Coating/Paint System

According to the report by Ramesh *et al.*, (2011), coating materials consist of binder, pigment, extenders and additives. A similar report by Grundmeier *et al.*, (2000) states that the organic coatings consist of a binder or vehicle, pigments, and additives such as dryers, hardening agents, stabilizing agents, surface activating compounds, and dispersion agents. The basic physical and chemical properties of the coating can be determined using the relatively low molecular weight type of polymers. However, the addition of pigments can significantly influence the properties of the coating. The pigments provide colour, act as a barrier for corrosive species and to serve as actively corrosion inhibiting species. Nowadays, metallic coatings such as zinc or zinc alloys are usually been used to cover the surface of steel. Grundmier and coworkers studied the formation and properties of surface conversion layer on zinc coated steel which the inorganic conversion layer is deposited on top of the metallic coating to generate a corrosion resistant interface and to provide a network to the organic primer. In automotive applications such as automotive radiators, cathodic electrocoat usually been used as a corrosion resistant organic primer. The topcoat gives the system its appearance and acts as a barrier between the corrosive medium and the inner layers. The primer and the topcoat both contain corrosion active pigments.

Protecting reactive metals by covering their surface with organic coatings is a smart way to take advantage of mechanical properties of metals such as steel or aluminium while preventing them from corrosion and introducing one or multiple requested surface properties in one step. These properties might be colour, wear resistance, formability, noise reduction and electronic insulation.

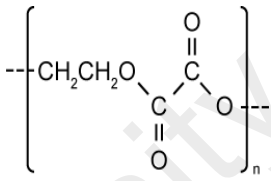
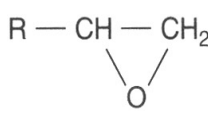
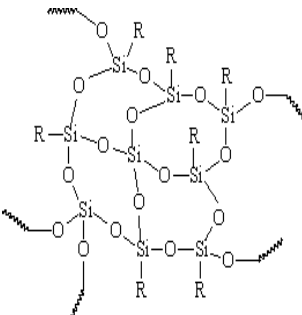
2.1.2 Organic and Synthetic Resins

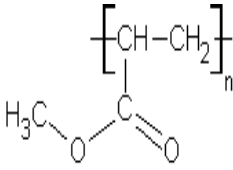
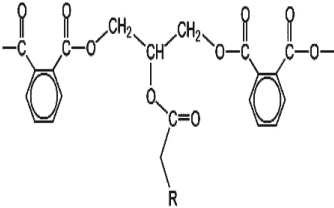
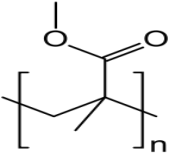
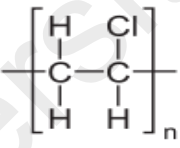
A great variety of synthetic resins are available, but only a few have been used in antifouling paints. Probably, many more are now being tested in various industrial laboratories. Alkyd resins have been used extensively in preparing paint coatings. In the underwater paint field, their use has been largely restricted to the anticorrosives and primers. They have not been used as the binder of continuous contact paints. Their inclusion in the proper proportions in resin base, soluble matrix type paints may give desirable film characteristics. The softer grades have been used as plasticizers in antifouling paints, and the harder grades have been mixed with resin or with drying oils to form the binder. Phenolic resins, modified with resin, have been used in hot melts and solvent type antifouling paints. Frequently, phenol and formaldehyde, together with lead acetate as a catalyst, are reacted in the presence of resin during the varnish cook. The resin obtained is less soluble in sea water than resin alone. The use of resin esters in place of the resin, though common in the manufacture of varnishes where water resistance is desirable, is generally not satisfactory for antifouling coatings (Woods Hole Oceanographic Institution (WHOI), 1952).

Organic coatings are the cheapest and easiest method for this purpose. Various types of organic resins (Erich *et al.*, 2005; Gite *et al.*, 2010; Rossi *et al.*, 2006) resins have been used for coating purposes in the past few decades. Among these, silicone resins have good resistance for corrosion in all kinds of environments and better thermal stability owing to their exclusive organic -inorganic hybrid molecular formation (Erich *et al.*, 2005; Ramesh *et al.*, 2007; Rossi *et al.*, 2006). Epoxy resin has good toughness, adhesion and chemical resistance, but, thermal and mechanical properties are not adequate for the applications in structural products (Rossi *et al.*, 2006). Silicone resins

have good compatibility with organic resins for modification. They have superior thermal properties such as higher thermo-oxidative stability. The hybrid coating system can protect the surface more efficiently (Ramesh *et al.*, 2007). The corrosion protection ability also can be enhanced by blending more than one organic resin. (Cao *et al.*, 2001; Anand Prabu and Alagar, 2004; Mafi *et al.*, 2008; Patil *et al.*, 2012; Ramesh *et al.*, 2011; Ramesh *et al.*, 2013). Table 2.1 below shows the common types of polymer resin used in the various coating systems and their properties.

Table 2.1: Common types of resin used in various coating systems

| Types of Resin | Chemical Structure | Properties | Examples of polymer resin based coating system (references) |
|----------------|---|--|---|
| Polyesters |  | <ul style="list-style-type: none"> -popular in appliance finishes. -low toxicity level -outstanding mechanical and chemical properties -good corrosion resistance | <ul style="list-style-type: none"> Ramesh <i>et al.</i>, 2011 Jahani, 2007 Parra <i>et al.</i>, 2002 Mafi <i>et al.</i>, 2008 Cao <i>et al.</i>, 2001 Naderi <i>et al.</i>, 2004 Prosek & Thierry, 2004 |
| Epoxy |  | <ul style="list-style-type: none"> -strong adhesive -excellent hardness but brittle -low volatility -good corrosion resistance | <ul style="list-style-type: none"> Liu <i>et al.</i>, 2005 Mafi <i>et al.</i>, 2005 Lange <i>et al.</i>, 2006 Barletta and Bellisario, 2011 Barletta <i>et al.</i>, 2012 Mirabedini <i>et al.</i>, 2003 Pearson & Yee, 1989 Patil <i>et al.</i>, 2012 |
| Silicone |  | <ul style="list-style-type: none"> -modified alkyds, acrylic and polyesters. -very high performance on most properties -pressure-sensitive adhesives -high heat resistance | <ul style="list-style-type: none"> Ramesh <i>et al.</i>, 2013 Anand Prabu & Alagar, 2004 Ananda Kumar <i>et al.</i>, 2006 Vengadaesvaran <i>et al.</i>, 2013 Ananda Kumar & Sasikumar, 2010 |

| | | | |
|----------------------------|---|---|--|
| Acrylic |  | <ul style="list-style-type: none"> -popular for automotive and general use -flexible and shock resistant than glass -easily cleaned -corrosion resistance and good insulator -high heat resistance and impact resistance | <p>Vengadaesvaran <i>et al.</i>, 2013 Gratzl <i>et al.</i>, 2014 Negm <i>et al.</i>, 2014 Huybrechts & Tanghe, 2007 Fay <i>et al.</i>, 2013 Sathiyarayanan <i>et al.</i>, 2007 Santana <i>et al.</i>, 2012</p> |
| Alkyd |  | <ul style="list-style-type: none"> -High electrical resistance -may be hard, rigid, soft, flexible and rubbery -used in paints and in moulds for casting -most commercial "oil-based" coatings | <p>Erich <i>et al.</i>, 2008 Azimi <i>et al.</i>, 2013 Ang & Gan, 2012 Atta <i>et al.</i>, 2013 Uzoh <i>et al.</i>, 2013 van Haveren <i>et al.</i>, 2007</p> |
| Poly (methyl methacrylate) |  | <ul style="list-style-type: none"> -economical alternative to polycarbonate -moderate properties, easy handling and processing and low cost. -brittle when loaded -modified PMMA can achieve high scratch and impact resistance | <p>Alemdar <i>et al.</i>, 2007 Jiang <i>et al.</i>, 2010 Hosseini <i>et al.</i>, 2014 Lewis <i>et al.</i>, 2009 Walsh & Frances, 2003</p> |
| Polyvinylchloride (PVC) |  | <ul style="list-style-type: none"> -strong, lightweight, durable -may be rigid or flexible, depending on the added compounds -good toughness, strength -flame resistant and fire prevention properties -excellent electrical insulation properties | <p>Castela <i>et al.</i>, 2000 Es-Sahebet <i>et al.</i>, 2012 Conradi <i>et al.</i>, 2012 Olad and Nosrati, 2013</p> |

2.1.3 Pigments

Pigments have been used more than 30,000 years ago in paintings. The paintings were produced in black, red, and yellow, created by various pigments available from their natural habitat, such as iron oxides, manganese oxides, chalk, and charcoal (Erich *et al.*, 2008). Pigments are still used today for aesthetic reasons; however, nowadays

more factors have to be considered. The coating in which the pigments are dispersed should protect the underlying substrate. In some cases the pigments even inhibit corrosion of metal substrates (Hare and Kurnas, 2000).

Most contemporary antifouling formulations employ an active pigment and a variety of organic or organo-metallic booster biocides which are embedded in, or linked with, an organic matrix. Cuprous oxide (Cu_2O) is the usual choice of pigment, although Cu(I) thiocyanate and Zn(II) oxide are also commonly employed (Nimisha Singh and Andrew Turner, 2009). For the corrosion protection effects, the analyses done by Ramesh *et al.*, (2013) reported that the best performing binder system would be identified and TiO_2 pigment added to that binder.

The level of pigmentation varies in different types of alkyd coatings. Obviously, the properties of a coating are influenced by the pigment volume concentration (PVC). The level of pigmentation depends on the requirements, such as costs, viscosity, gloss, hardness, chemical resistance, etc. However, by changing the level of pigmentation, the protective properties of the coating are also altered, making optimization of a coating formulation a complex process. As a result, many studies have been carried out to understand the effect of pigments on the paint properties (Bierwagen and Mallinger, 1982; Bierwagen and Rich, 1983; Tiarks *et al.*, 2002; Perera *et al.*, 2004, Erich *et al.*, 2008). The level of pigmentation is characterized by the pigment to volume concentration, defined by

$$PVC(\%) = \frac{V_p}{V} \times 100 \text{ ----- Equation 1}$$

Where V_p is the volume of the pigment and V is the volume of the dry coating (the sum of the volume of the pigment and the binder). It has been found that a critical pigment to

volume concentration (CPVC) exists, which corresponds to the point at which there is just enough binder in the dry coating to completely fill all the voids between the pigment particles (Asbeck and Loo, 1949; Erich *et al.*, 2008).

2.1.4 Solvents

In paints/coating system, the use of solvent is beneficial for dissolve or dispersal of different component used in the paint formulation such as pigment and resin for application. After the paint is applied, the solvent will evaporates and this will allow the resin and pigment to produce a film of paint (a coat) and cured rapidly. In the work done by Shi *et al.*, (2009), acetone was chosen as the solvent in the epoxy composites coating development.

Common types of solvent used in coating/paint systems are toluene (Khorasani *et al.*, 2005; Jawalkar *et al.*, 2007; Ulyana Kharchenko and Irina Beleneva, 2013; Christine Bressy and André Margailan, 2009), xylene, (S. Sathiyarayanan *et al.*, 2008; Ramesh *et al.*, 2013, Jamari *et al.*, 2013), acetone (Willi Schlesing *et al.*, 2004), and etc.. Burgentzle *et al.*, (2004) in their report listed different solvents been used in their work (Table 2.2).

Table 2.2: Solubility parameters and surface energies of the different solvents

| Solvent | δ (MPa ^{1.5}) | δ_H (MPa ^{1.5}) | $\gamma_{L/V}$ (mN m ⁻¹) |
|--|-----------------------------------|-------------------------------------|---|
| Ethyl alcohol | 26.0 | 19.4 | 22.8 |
| Acetone | 20.1 | 7.0 | 23.7 |
| Ethyl acetate | 18.2 | 5.1 | 23.9 |
| Butane 1-ol | 23.1 | 15.8 | 24.6 |
| Methyl ethyl ketone | 19.0 | 7.2 | 24.6 |
| Cyclohexane | 16.8 | 0.2 | 25.5 |
| Chloroform | 19.0 | 5.7 | 27.1 |
| Toluene | 18.2 | 2.0 | 28.5 |
| Ethylbenzene | 17.8 | 1.4 | 29.2 |
| Xylene | 18.0 | 3.1 | 30.1 |
| Ethylene glycol monobutyl ether ^a | 20.9 | 12.3 | 31.3 |
| Ethyl acetoacetate | 20.1 | 10.2 | 32.5 |
| Diethylene glycol monobutyl ether ^b | 24.6 | 15.6 | 35.4 |
| Dimethylformamide | 24.8 | 11.3 | 35.8 |
| Benzyl alcohol | 23.3 | 13.7 | 39.0 |

According to Woods Hole Oceanographic Institution (WHOI) in 1952, an antifouling paint should be designed to allow the application of paint on the vessel wherever it is convenient to dock them and by whatever labor is available. The paint properties should not be seriously altered by wide variations of temperature for the ease of application since vessels must be painted in all seasons and climates. In cold weather, the paint formulation becomes undesirably thick. To prevent this situation, it should be formulated so that solvents available are suitable for thinning.

2.1.5 Hardener and Additives

The addition of hardener and/or additives can improve the performance of antifouling and anti corrosion properties of coatings. The addition of polyisocyanate (NCO) hardener with silicone and polyester resins would have enhanced the further molecular interactions and made more Si-C, Si-O-Si functional groups which possess higher thermal stability (Ramesh *et al.*, 2013).

Research done by Huybrechts and Tanghe, (2007) also reported the hardener used influenced the glass transition, T_g , which leads to early drying performance and hardness of the coating.

The addition of an enzyme complex as biocomponent additive to the vinyl chloride–vinyl acetate copolymer UM50 based coating makes a coating system susceptible to corrosion damage. Kharchenko and Beleneva, (2013) have used polyamine type hardener as the curing agent.

The reinforcement of a coating material can be achieved using nanoclay/ polymer composite materials (Chan *et al.*, 2011). Sathiyarayanan *et al.*, (2008) in their work

used polyaniline glass flake composite to improve the corrosion resistance performance of the coating. The addition of SiO₂ nanoparticles was also found to significantly improve the microstructure of the coating matrix and thus enhanced both the anticorrosive performance and Young's modulus of the epoxy coating (Shi *et al.*, 2009).

2.2 Coatings on Steel Substrates

Coating resistance, R_c has been generally interpreted as the pore resistance of the coating resulting from the penetration of the electrolyte. Electrolyte penetration may occur through real (microscopic) pores and/or virtual pores defined by regions in the polymer of low crosslinking and therefore high transport.

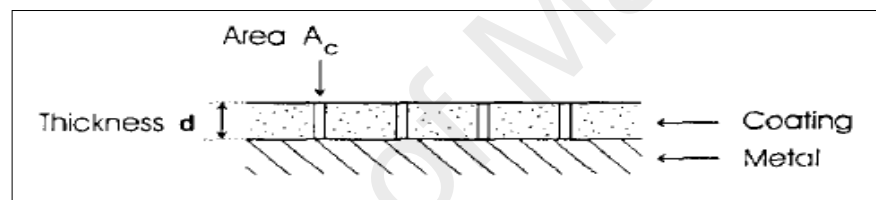


Figure 2.2: Diagram of coating on a metal plate. (Amirudin and Thierry, 1995)

R_c can be related to the number of pores or capillary channels perpendicular to the substrate surface through which the electrolyte reaches the interface as follows:

$$R_c = d/\sigma N A_c \quad \dots\dots\dots \text{Equation 2}$$

where σ is the conductivity of the electrolyte, N is the number of channels, A , is the average cross-sectional area of the channels and d is the length of the channels which is equal to the coating thickness.

2.2.1 Atmospheric Corrosion

The term “atmospheric corrosion” comprises the attack on metal exposed to the air as opposed to metal immersed in a liquid. Atmospheric corrosion is the most prevalent type of corrosion for common metals.

Corrosion is defined as the destruction of materials caused by chemical or electrochemical action of the surrounding environment. This phenomenon is experienced in day to day living. The most common examples of corrosion include rusting, discoloration and tarnishing. Corrosion process can be conveniently classified as follows.

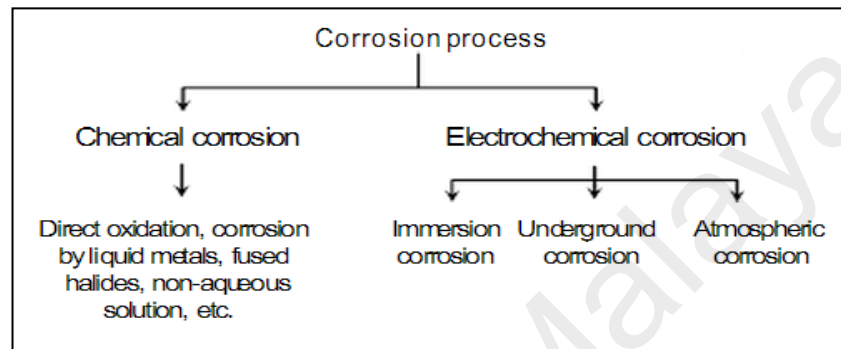


Figure 2.3: Classification of Corrosion Process (Syed, 2006)

For atmospheric corrosion in near-neutral electrolyte solution, the oxygen reduction reaction is applicable in cathodic process (Zou *et al.*, 2011; Syed, 2006):



The anodic process: Equation represents the generalized anodic reaction that corresponds to the rate-determining step of atmospheric corrosion.



The corrosiveness of a marine environment depends on the topography of the shore, wave action at the surf line, prevailing winds and relative humidity. Marine atmospheres are usually highly corrosive. Chloride ion derived from sodium chloride of seawater is the main active agent for corrosion initiation (Syed, 2006).

Besides the need to assure efficient anticorrosive protection painting that is compatible with cathodic protection, it is also necessary to keep the surface as smooth as possible in order to minimise drag resistance when the ship is in movement and thus reduce fuel consumption which means the need to prevent the attachment of a wide variety of marine organisms, both plants (flora) and animals (fauna). Furthermore, in recent decades the antifouling paints applied on ship hulls must not only prevent the fouling of underwater areas but must do this in compliance with emerging regulations and legislation and furthermore are required not to release harmful biocides into the sea water. Thus, a fight against time is on demanded by the International Maritime Organization, IMO in an ongoing search for practically “miraculous” antifouling products. Figure 2.4 summarises a series of interactions between ship hulls and seawater (Almeida *et al.*, 2007).

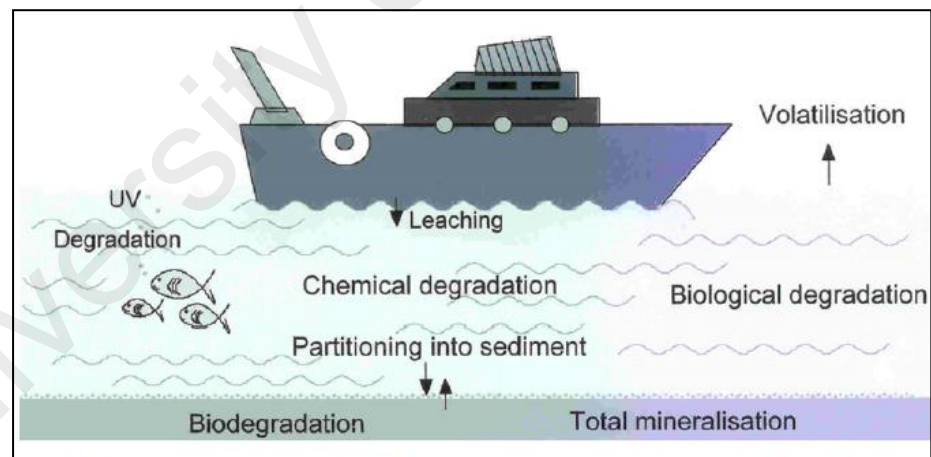


Figure 2.4: Fate of active ingredients of antifouling paints in seawater (Almeida *et al.*, 2007)

2.3 Anticorrosion Coatings

An anticorrosion coatings or corrosion resistant coatings protect metal components against degradation due chemical reaction with their environment. The metals are damaged by the formation of unusable metal oxides by corrosion. The increase in the

material cost gives an alarmic awareness to protect the existing metals used in industries, bridges, buildings and other places from the adverse effect of corrosion. Previously, cathodic protection, alloying, metal coatings and organic coatings have been applied to protect the metal surface (Wicks *et al.*, 1999; Ananda *et al.*, 2006; Ananda and Sasikumar, 2010; Grundmier *et al.*, 2000; Ramesh *et al.*, 2011; Ramesh *et al.*, 2013). There are a lot of improvements in the materials and methods to achieve perfect anticorrosive system.

In protective coatings, the coating resistance, R_c can be classified into a few types which are good, fair and poor (Bacon *et al.*, 1948, Greenfield and Scantlebury, 2000; Rau *et al.*, 2011). Figure 2.5 below illustrated the three general classification of resistance value that established during investigation.

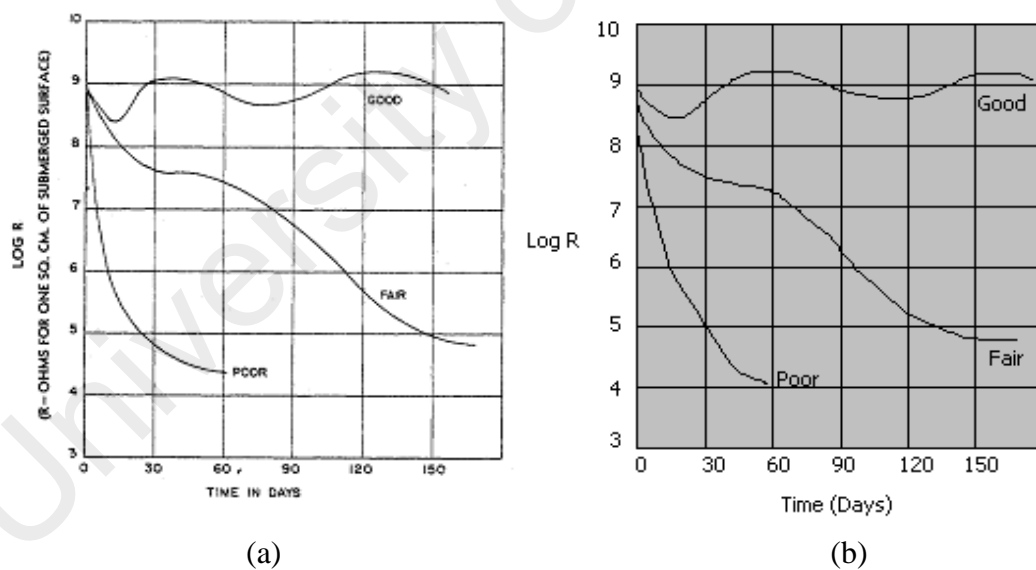


Figure 2.5: The schematic value for good, fair and poor of coating resistances; (a) Bacon *et al.*, 1948 and (b) Greenfield and Scantlebury, 2000.

2.3.1 Biofouling

Marine biofouling is a natural phenomenon representing one of the greatest problems in marine technology and navigation, since the accumulation of organisms such as barnacle, tube worms and algae on the submerged surfaces of the vessels results in important speed reduction and considerably higher fuel consumption. (Chambers *et al.*, 2006; Woods Hole Oceanographic Institution (WHOI), 1952; Oikonomou *et al.*, 2012).

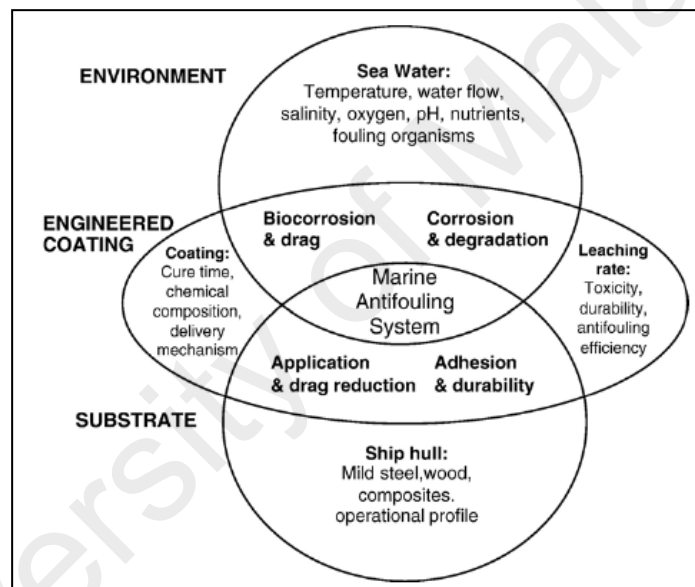


Figure 2.6: Parameters that affecting antifouling system (Chambers *et al.*, 2004).

Biofouling also exploits ecological niches on a ship's hull, generating varying settlement densities. This can lead to propeller fouling and the water line fouling. Effect on vessel's sound signature can also be affected, by this degradation of a ship's performance, for both passive and active sonar systems (Chambers *et al.*, 2006). They also reported on the requirements of an optimal antifouling coating that listed in Table 2.3 below.

Table 2.3: Requirements of an optimal antifouling coating (Chambers *et al.*, 2006)

| Must be: | Must not be: |
|---|-----------------------------------|
| Anticorrosive | Toxic to the environment |
| Antifouling | Persistent in the environment |
| Environmentally acceptable | Expensive |
| Economically viable | Chemically unstable |
| Long life | A target for non-specific species |
| Compatible with underlying system | |
| Resistant to abrasion/biodegradation/erosion | |
| Capable of protecting regardless of operational profile | |
| Smooth | |

The adhesion of species to a substrate is an important aspect of biofouling. If this process could be prevented, fouling could be controlled. The use of antifouling paints on ship hulls has been an historic method of controlling biofouling (Yebra, *et al.*, 2004; Boopalan and Sasikumar, 2011).

2.3.2 Types of Biofouling

“*Marine Fouling and its Prevention*” by Woods Hole Oceanographic Institution (WHOI) in 1952 reported that nearly 2000 species had been identified on fouled structures later increased the number to more than 4000 species. Nevertheless, it still includes a very small proportion of the known marine species. Marine structures at platforms, jetties and ship hulls are subject to diverse and severe biofouling. Almeida *et al.*, (2007) and Chambers *et al.*, (2006) in their report showed the stages of biofouling activities by marine organism when immersed in seawater.

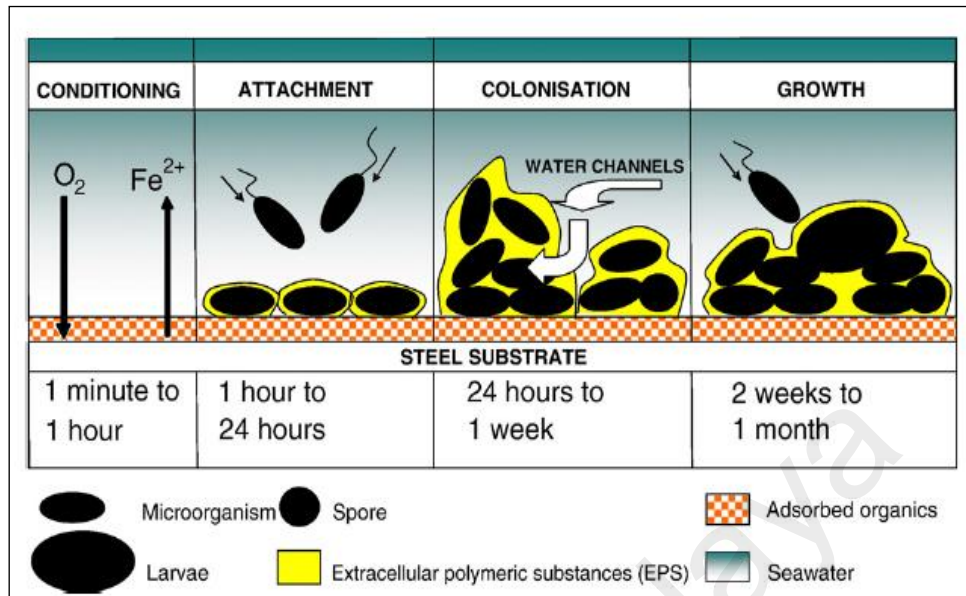


Figure 2.7: Diagram of critical biofouling stages (Chambers *et al.*, 2006)



















Table 2.4: Stages of attachment of marine organisms on surfaces immersed in seawater (Almeida *et al.*, 2007)

| Processes involved | Attached organisms | Nature of film formed | Approximate initiation time |
|--|---|--|-----------------------------|
| Stage 1 Essentially physical forces, such as electrostatic interactions, Brownian movement and Van der Waals forces | "Adhesion" of organic molecules, such as proteins, polysaccharides and proteoglycans and, possibly, some inorganic molecules | Conditioner | 1 min |
| Stage 2 Reversible "adsorption" of mentioned species, especially by physical forces, and their subsequent adhesion interacting together with protozoans and rotifers | Bacteria, such as <i>Pseudomonas putrefaciens</i> and <i>Vibrio alginolyticus</i> and diatoms (single-cell algae) such as <i>Achnantes brevipes</i> , <i>Amphora coffeaeformis</i> , <i>Amphiprora paludosa</i> , <i>Nitzschia pusilla</i> and <i>Licmophora abbreviata</i> | Microbial biofilm | 1–24 h |
| Stage 3 Arrangement of microorganisms with greater protection from predators, toxicants and environmental alterations, making it easier to obtain the nutrients necessary for the attachment of other microorganisms | Spores of microalgae, such as <i>Ulothrix zonata</i> and <i>Enteromorpha intestinalis</i> , and protozoans, including <i>Vaginicola</i> sp., <i>Zoothamnium</i> sp. and <i>Vorticella</i> sp. | Biofilm | 1 week |
| Stage 4 Increase in the capture of more particles and organisms, such as the larvae of marine macroorganisms, as a consequence of the pre-existence of the biofilm and the roughness created by the irregular microbial colonies that comprise it | Larvae of macroorganisms, such as <i>Balanus amphitrite</i> (Crustacea), <i>Laomedea flexuosa</i> (Coelenterata), <i>Electra crustulenta</i> (Briozoa), <i>Spirorbis borealis</i> (Polychaeta), <i>Mytilus edulis</i> (Mollusca) and <i>Styela coriacea</i> (Tunicata) | Film consisting of the attachment and development of marine invertebrates and growth of macroalgae (seaweed) | 2–3 weeks |

In 2004, Yebra *et al.* reported that the local severity of biofouling depends upon a large number of parameters. The water conditions, dependent on the geographical location and the operating pattern of the vessel are some of these parameters. Consequently, these parameters cannot be modified to control the growth of the fouling organisms. They also reported on the general stages of the compounds that are rapidly accumulated on every surface which give rise to the so-called conditioning film.

In 2007, Almeida and co-workers reported on the variation of marine organisms that have been subjected to specific research. They have listed certain characteristics of the main species of macroorganisms as in Table 2.5 below.

Table 2.5: Characteristics of main marine macroorganism species (Almeida *et al.*, 2007)

| Groups | Algae (plants) | Invertebrates (animals) | | | | | | | |
|---------------------------|--|---|---|---|---|--|---|---|---|
| Subgroups | (a) green, (b) brown and (c) red | Hard shell organisms | | | | Grass type organisms | Small bush organisms | Spineless organisms | |
| Designation | (a) <i>Enteromorpha</i> , <i>Ulva</i> and <i>Cladophora</i> , (b) (<i>Ectocarpus</i> and <i>Fucus</i> , and (c) (<i>Ceramium</i>) | <i>Balanus</i> | <i>Barnacles</i> | <i>Molluscs</i> | <i>Fouling bryozoans</i> | <i>Hydroids or bryozoans</i> | <i>Hydroids or bryozoans</i> | <i>Ascidians</i> | <i>Sponges and sea anemones</i> |
| Example of typical aspect |  |  |  |  |  |  |  |  |  |
| Designation | <i>Green algae</i> | <i>Balanus</i> | <i>Calcareous polychaetes</i> | <i>Molluscs</i> | <i>Fouling bryozoans</i> | <i>Bryozoans</i> | <i>Bryozoans</i> | <i>Ascidians</i> | |
| Example of typical aspect |  |  |  |  |  |  |  |  |  |
| Short description | Only plants that become attached to immersed surface: a) close to surface; b) at mid depth; and c) at depth | Attached trunc-conical or cylindrical crustaceans | Barnacles are <i>Balanus</i> that are fixed to surfaces via a stem | Bivalves containing a spineless animal in their interior | Calcareous incrustations that multiply from a central individual | Organisms that cover surfaces with an open grass or fur | Like bushes of several centimetres and with branches | Constituted by a spineless bag with two tubular openings or starry plates | Spineless and spongy aspect (sponges) and sea anemones |

2.4 Characterization of Antifouling Coatings

2.4.1 Antifouling Properties

The composition and development of antifouling coatings are generally recognized and have agreed to in accordance with the needs of their quality. But, there are so little agreement and discussion on this matter. The lack of understanding and failure to understand the antifouling action will results empirical and sometimes irrational approach to the problem. This topic discussed the solution of these difficulties by stating the problems, defining them in necessary terms, describing the formulation, and summarised the common important properties used in the antifouling coatings.

2.4.2 Effects on Corrosion

In the application of ship bottom paint system, it is essential that the steel vessel/ship hull to be protected from corrosion effect. The rusting prevention of the coating material is a must since it can results fouling on the coated surface if it is not been prevented. The effectiveness of this anticorrosive behavior may determine the success of the antifouling material (Woods Hole Oceanographic Institution (WHOI), 1952). A wide range of exposure condition of a large ship will gives rise to a complexity and diversity of anticorrosive protection situation and this phenomenon need to be resolved. The areas of protection include the hull, deck, superstructures, fuel tanks, ballast tanks, and others (Almeida *et al.*, 2007). According to Ramesh *et al.*, (2007), corrosive environment need to be evaluated to study the protection ability of a coating system.

Corrosion resistance behavior can be studied by running the impedance measurement using Electrical Impedance Spectroscopy or known as EIS (Amirudin and Thierry, 1995;Sathiyarayanan *et al.*, 2007; Ramesh *et al.*, 2007; Ananda Kumar and

Sasikumar, 2010; Patil *et al.*, 2012; Kharchenko and Beleneva, 2013; Ramesh *et al.*, 2013). Figure 2.8 show examples of bode plots obtained from the EIS measurement.

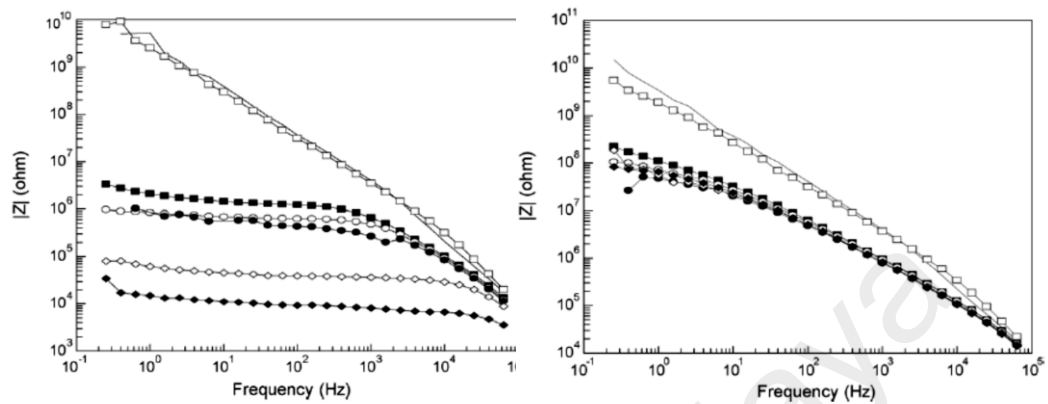


Figure 2.8: Example of Bode plot of glass flake containing paint coated steel in artificial seawater over time (Sathiyarayanan *et al.*, 2008)

Table 2.6 and Table 2.7 below show the impedance data obtained from the EIS measurement for the glass flake and polyaniline glass flake composite coatings (PGFC) (Sathiyarayanan *et al.*, 2008) and coating resistance (R_c) value obtained of polyester/epoxy powder coatings after 7 days and 50 days immersion in 3.5% NaCl artificial seawater solution (Mafi *et al.*, 2008).

Table 2.6: Coating resistance, R_c of glass flake and polyaniline glass flake composite coatings on steel in artificial seawater (Sathiyarayanan *et al.*, 2008)

| Time (days) | Glass flake | | PGFC | |
|-------------|---|---|---|---|
| | Coating resistance, R_c ($\Omega \text{ cm}^2$) | Coating capacitance, C_c (F cm^{-2}) | Coating resistance, R_c ($\Omega \text{ cm}^2$) | Coating capacitance, C_c (F cm^{-2}) |
| 0 | 2.71×10^{10} | 5.63×10^{-11} | 1.24×10^{11} | 3.29×10^{-11} |
| 1 | 3.39×10^8 | 6.03×10^{-10} | 3.69×10^{10} | 4.48×10^{-11} |
| 4 | 1.13×10^9 | 8.71×10^{-10} | 6.93×10^9 | 1.00×10^{-11} |
| 8 | 2.79×10^4 | 4.35×10^{-10} | 1.83×10^7 | 1.39×10^{-9} |
| 16 | 8.53×10^4 | 2.29×10^{-10} | 8.08×10^8 | 5.14×10^{-10} |
| 30 | 1.03×10^5 | 3.28×10^{-10} | 1.28×10^8 | 4.58×10^{-10} |

Table 2.7: Coating resistance, R_c value obtained for polyester/epoxy powder coatings after 7 days and 50 days immersion in 3.5% NaCl solution (Sathiyarayanan *et al.*, 2008)

| Immersion time (days) | Coating resistance (R_p) ($\Omega \text{ cm}^2$) | | Coating capacitance (C_c) (F/cm^2) | |
|-----------------------|--|-----------------|---|-----------------|
| | Polyester | Polyester/epoxy | Polyester | Polyester/epoxy |
| 7 | 5.51E+07 | 2.30E+08 | 3.30E-10 | 9.00E-11 |
| 50 | 4.65E+04 | 4.27E+05 | 2.90E-09 | 1.27E-09 |

2.4.3 Durability

The durability of a coating mainly depends on the mechanical damage resistance. Other than that, the softening effect due to water movement on the coated surface may vary the durability of a coating. The toxicity and durability need to be considered since the coatings will slowly dissolve to permit the liberation of the toxic (Bressy and Margailan, 2009; Buma *et al.*, 2009; Ramesh *et al.*, 2013; Woods Hole Oceanographic Institution (WHOI), 1952). The efficiency of an antifouling coating through a long term period can be achieved by properties such as antifouling protection in stationary conditions, constant leaching rate, the polishing rate with sailing speed and appearance or physical effect of a leached layer (Singh and Turner, 2009; Daffron *et al.*, 2011; Oikonomou *et al.*, 2012; Chen *et al.*, 2013).

The commercial paints have an average effectiveness of three to six months under subtropical fouling conditions (Woods Hole Oceanographic Institution (WHOI), 1952). Researchers need to develop effective antifouling coatings with longer periods and for different environmental conditions.

2.4.4 Adhesion

In shipbuilding industry, a coating must adhere to the wood or steel of the ship's bottom. A good coating must have good adhesion to the substrate. The coating should

adhere well when applied under certain condition especially under different kind of environment particularly during winter. Besides that, a coating with good mechanical strength in terms of impact resistance and coating with good thermal stability will also give rise to the proper adhesion of coating (Niu *et al.*, 2010; Ramesh *et al.*, 2013; Selvaraj *et al.*, 2009; Mafi *et al.*, 2008; Anand Prabu and Alagar, 2004; Parra *et al.*, 2002).

2.4.5 Surface Properties

The surface properties of coatings can be determined by a few methods. In 2011, Barletta and Bellisario have conducted progressive mode scratch tests with a surface profile using Micro-Combi Tester for epoxy-polyester coatings deposited onto the untreated (NT), macro-roughened (T60) and micro-roughened (T80) and silicon pre-coated (S) stainless steel substrates. Figure 2.9 and Figure 2.10 show the SEM images for the progressive scratch test and the surface profile on untreated (NT) and treated (T60 and T80) stainless steel metal substrate respectively.

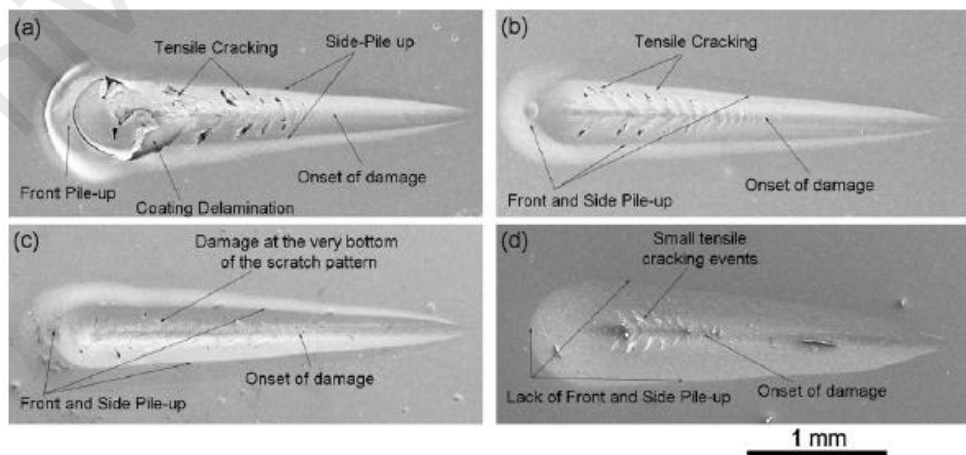


Figure 2.9: SEM images of residual scratch pattern after 0-30 N progressive load scratch test (Barletta and Bellisario, 2011)

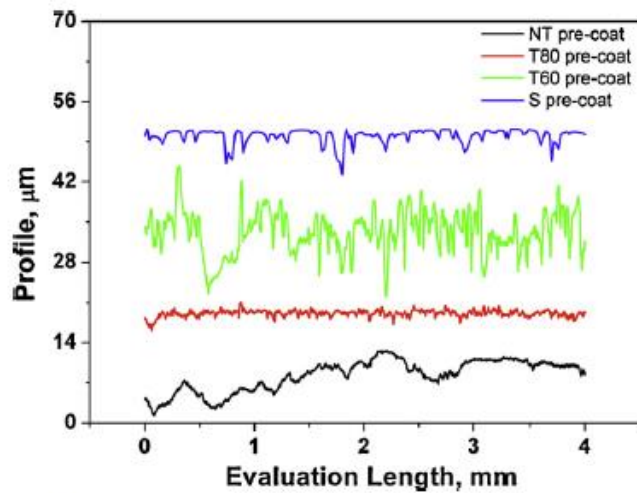


Figure 2.10: Surface profile on untreated (NT) and treated (T60 and T80) stainless steel metal substrate (Barletta and Bellisario, 2011)

Surface topography and roughness measurements also been reported by Barletta and coworkers in 2007 to study the surface appearance and wear resistance of the epoxy-based thermosetting powder coatings. Figure 2.11 and Figure 2.12 show the results of SEM images for different baking temperature and 3D film morphology of film status with different baking time and temperature of epoxy- based system with carboxylic acid-terminated polyester resins respectively.

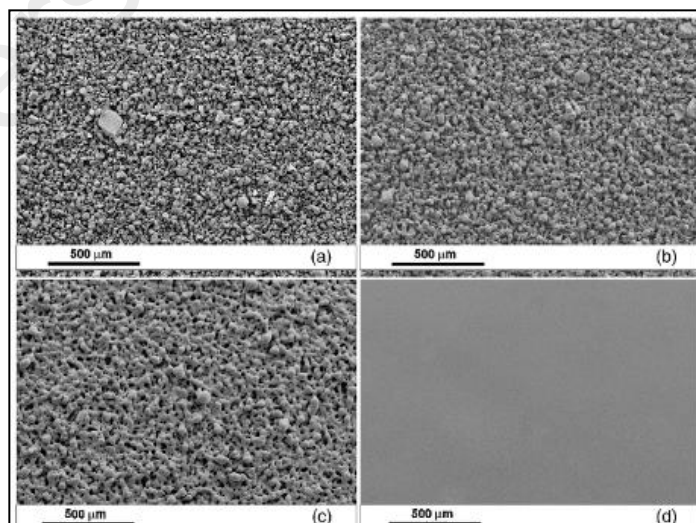


Figure 2.11: Levelling of the epoxy- based system with carboxylic acid-terminated polyester resins as cross-linkers onto coated metal substrate: SEM images at (a) 125 °C and 60s; (b) 150 °C and 60s; (c) 175 °C and 60s; (d) 200 °C and 60s (Barletta *et al.*, 2007)

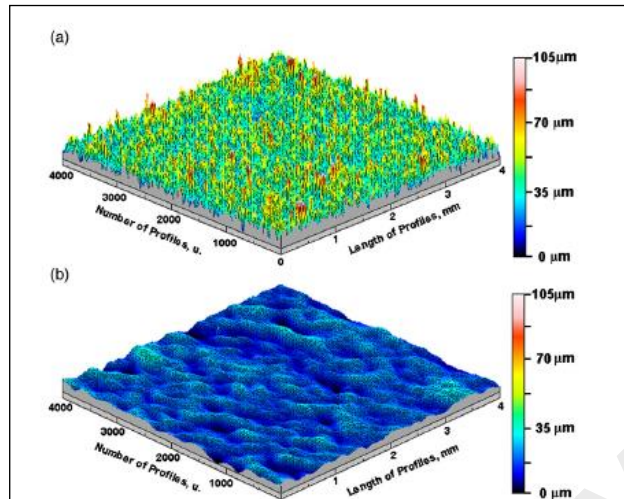


Figure 2.12: 3D maps of film morphology in the different status of: (a) loose (100 °C-1 min); (b) almost leveled (175 °C-1 min) powders (Barletta *et al.*, 2007)

From the available data, another type of surface characterization was done by the researcher to study the specular gloss and roughness effect with different baking time and temperature of the polymeric film. The results are shown in Figure 2.13 below.

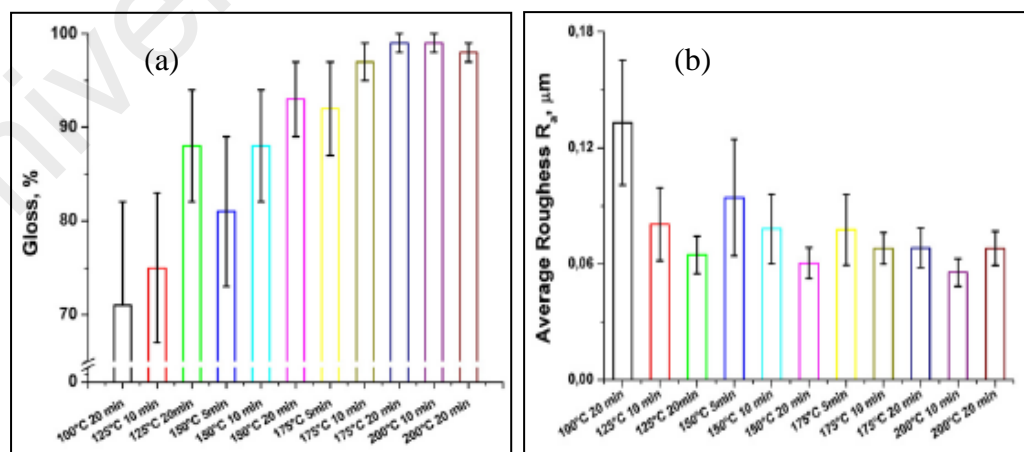


Figure 2.13: (a) Specular gloss and (b) average roughness of polymeric film at different long time baking condition (Barletta *et al.*, 2007)

The smooth and glossy surface will lead to better appearance of a coating film and reduced the surface roughness of coating surface (Ozcelik *et al.*, 2012; Dullaert *et al.*, 2011; Barletta *et al.*, 2007; Jarnstrom *et al.*, 2008). With the high reflection of an object to the surface, the more brilliant the coating film will appear (Yebra *et al.*, 2004; Woods Hole Oceanographic Institution (WHOI), 1952; Huybrechts and Tanghe, 2007). In other words, glossiness of the coated surface will help to enhance the surface properties of the coatings. However the roughening effect of the coated surface has promote better adhesion of the coating on the substrate.

In other reports by Erich *et al.* (2008), the pigment volume concentration (PVC) content in the coating system will gives different morphology and structure of the coated surface. The scanning electron microscope (SEM) images reveal that the higher PVC, the more porous structure will be produced. Up to 50% PVC, the smooth surface can be seen. However, with higher percentage of PVC, the porosity of the coated surface is observed with at PVC higher than 50%. Figure 2.14 below show the SEM images with different percentage of PVC added in the coating system.

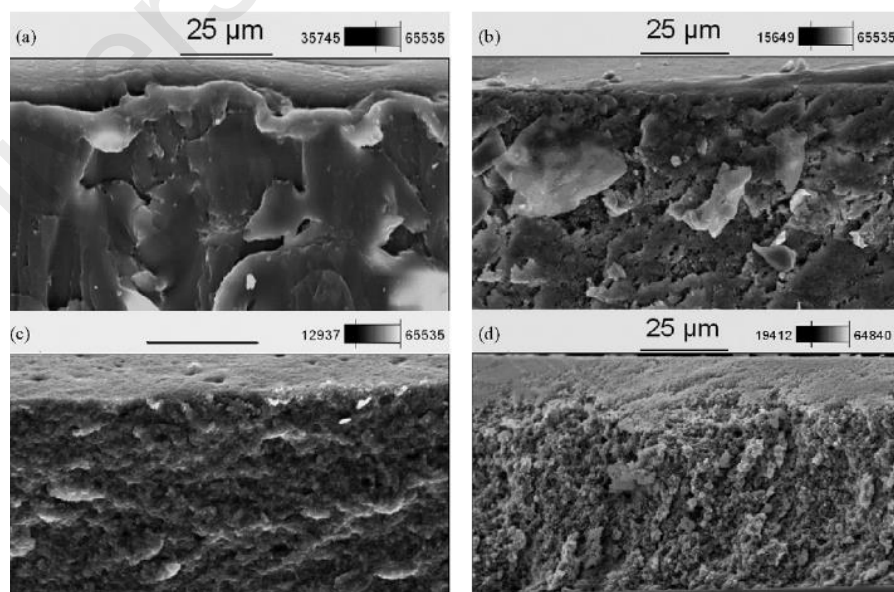


Figure 2.14: SEM images of cross-sections of coatings with (a) 0%, (b) 25%, (c) 50% and (d) 75% PVC. At the top of the images the coating surface is visible (Erich *et al.*, 2008)

2.4.6 Biocides Release

The release of biocides is one of the major aspects in preventing the biofouling activity on the marine hull. This can be determined by obtaining the leaching rates of the metal concentrations in solutions. Induced coupled plasma (ICP) has been used by other researchers to study the metal leaching concentration that can explain the effects of the biofouling on the coated surface and the importance of environmental and biological implications of antifouling residues in seawater (Singh and Turner, 2009; Schiff *et al.*, 2004; Costa *et al.*, 2013). Figure 2.14 and Figure 2.15 show the results obtained by researchers to study the metal leaching concentration using ICP on different conditions and types of vessels/hulls.

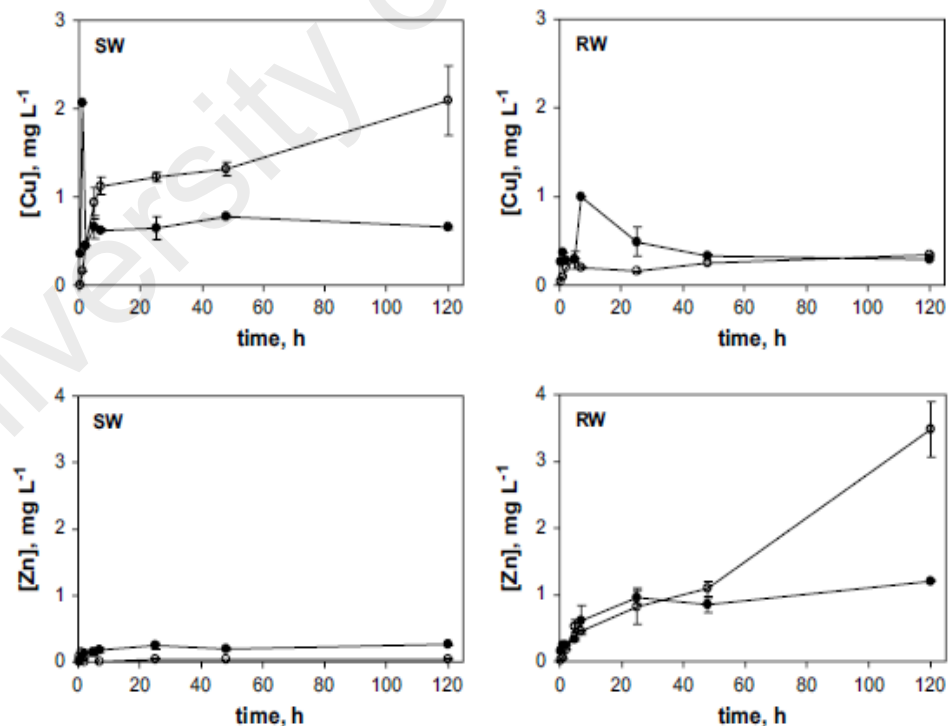


Figure 2.15: Time-dependant release of Cu and Zn in paint composite in seawater (SW) and river water (RW) and at 4 °C (○) and 19 °C (●) (Singh and Turner, 2009)

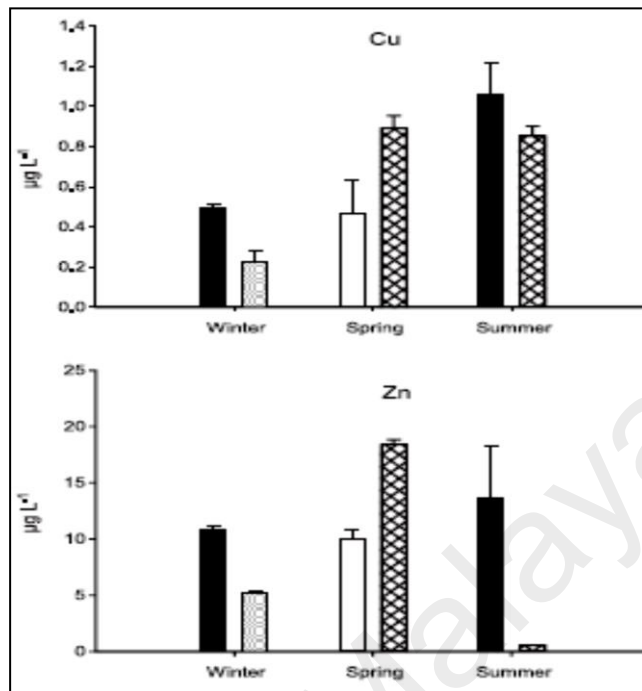


Figure 2.16: DGT-labile concentrations ($\mu\text{g/L}$) of copper and zinc in high-salinity (black bar), intermediate-salinity (hatched bar), and low-salinity (dotted bar) water and in fresh water (white bar) after 48 h of DGT deployment at the Santos Shipyard, Brazil (Costa *et al.*, 2013)

2.4.7 Antimicrobial Activity

In recent years, the antimicrobial activity study has been reported to describe the first step of biofilm formation on the surface of coatings (Gratzl *et al.*, 2014). Few types of microorganism have been used such as *Aspergillus Niger*, *E-Coli*, *S. Aureus*, *Pseudomonas aeruginosa* (Tomsic *et al.*, 2009; La Russa *et al.*, 2012; Kugel *et al.*, 2011; Kharchenko *et al.*, 2012; Singh *et al.*, 2013; Muñoz-Bonilla and Fernandez-Garcia, 2012) to investigate the microbial growth inhibiting properties or anti biofilm/fouling nature. One of the methods used to study the antimicrobial activity on the coating is the microorganism suspension method whereby a fixed amount and concentration of fungi/bacteria was spreaded on the nutrient agar on the petri dish and left at certain

temperature to observe the microorganism growth on the coating samples (Tomsic *et al.*, 2009; Wang *et al.*, 2012).

The antimicrobial activity test can be carried out with microorganism suspension method or also known as agar diffusion method in which the inhibition contact area of the microorganism can be determined. Report by Gratzl *et al.*, (2014) show that the inhibition contact area of antifungal activity of poly (acrylic acid) block copolymers against *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*. Figure 2.17 show the results of antimicrobial activity of poly(acrylic acid) block copolymers.

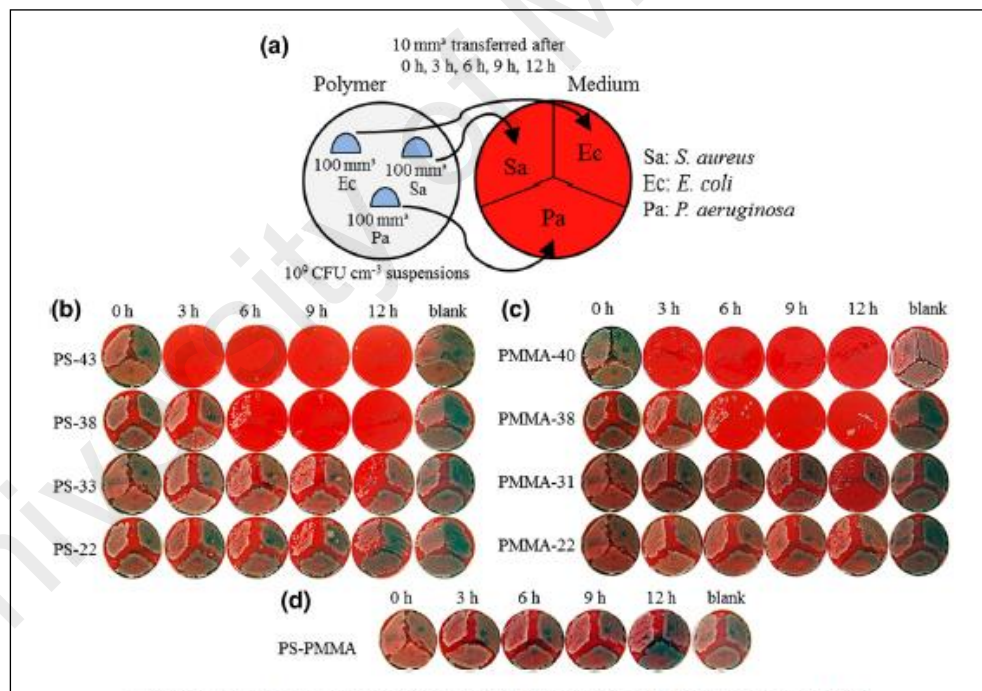


Figure 2.17: (a) Antimicrobial test procedure and results for (b) poly(styrene) - poly(acrylic acid) diblock copolymer (PS-b-PAA), (c) poly(methyl methacrylate)- poly(acrylic acid) diblock copolymer (PMMA-b-PAA), and (d) the reference polymer the poly(styrene)- poly(methylmethacrylate) diblock copolymer (PS-b-PMMA) (Gratzl *et al.*, 2014)

Another report by Tomšić *et al.*, (2009) shows the study of antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric on the coatings. In their report, various treated cotton fabrics was assessed before and after repetitive (up to 10x) washing by the application of standard tests: for the fungi *Aspergillus niger* (ATCC 6275) and *Chaetomium globosum* (ATCC 6205) by the modified DIN 53931 standard method. The growth of *Chaetomium globosum* after 7 days incubation at 29 °C on the variously treated cotton samples is shown in Figure 2.18.

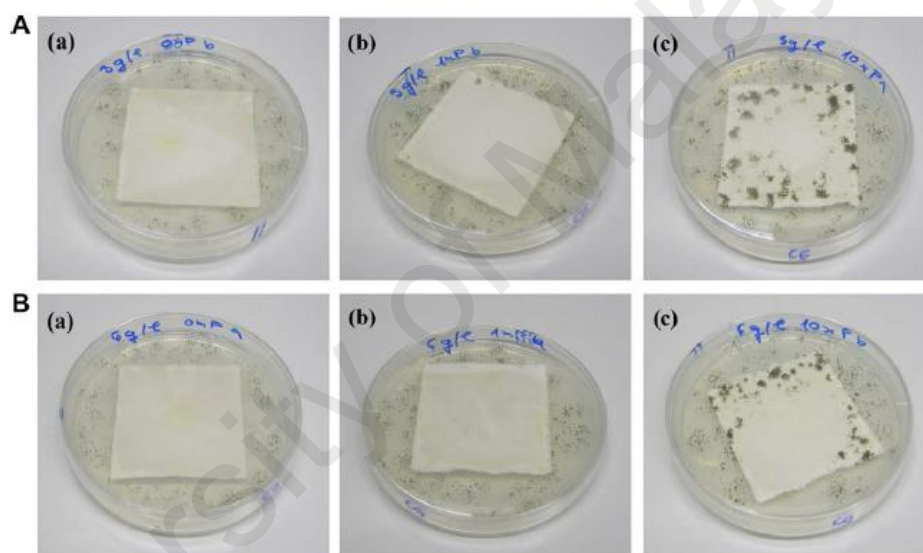


Figure 2.18: Growth of *C. globosum* on synthetic nutrient-poor agar (SNA) covered with finished samples E1 (A) and E2 (B); (a) unwashed, (b) washed once, (c) washed ten times

From the above results, it shows that the antifungal activity became effective when the Ag concentration on the cotton sample was higher than 100 ppm. The results also revealed that the antimicrobial activity of the coatings strongly depended on the concentration of Ag in the corresponding Ag-RB dispersions.

2.5 Summary

This chapter reviewed some of the antifouling characteristics that have been studied since 1950's. Various types of resins used as the binders in the antifouling systems have been briefly discussed. Different types of biocides (toxicants) used and the effects of the biocides release in the seawater were also reviewed in this chapter. The effects towards the surface of the developed antifouling coating systems have been listed. Since over last 50 years, there are major reviews on antifouling coatings that have led to the modern approaches and strategies to marine antifouling coatings (Chambers *et al.*, 2006; Dafforn *et al.*, 2011). They have listed the developments of antifouling strategies, the advantages and disadvantages of past and present antifouling coatings and discussed some modern approaches to replace the conventional coatings that can produce much better performance of antifouling coatings. Some characterizations and analyses on these antifouling coatings using electrical impedance spectroscopy (EIS), scanning electron microscopy (SEM), induced coupled plasma (ICP), antimicrobial activity and physical effect after immersion in seawater done by previous researchers were also briefly discussed.

CHAPTER 3: EXPERIMENTAL METHOD

3.0 Introduction

In this present work, copper and copper based antifouling coatings were developed and characterized using a sophisticated analytical methods and custom made field work apparatus. First stage of this project is to develop best performing binder system with optimum performance. This binder was then used to develop antifouling coatings using copper and copper oxide. Detailed flow chart was given below at Figure 3.1.

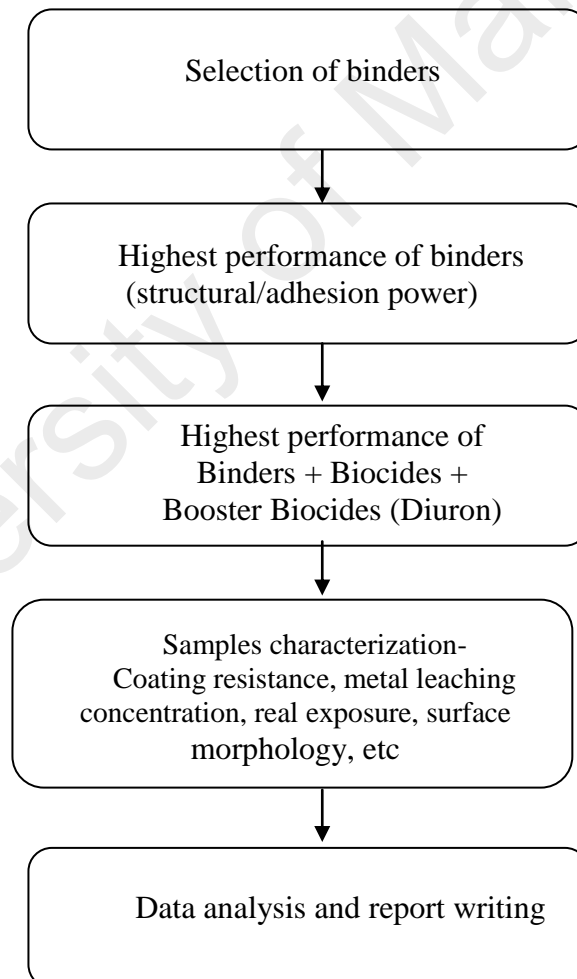


Figure 3.1: Flow chart of the research project

3.1 Samples preparation

3.1.1 Binder system

Binder system must possess good physical, mechanical, thermal and electrochemical properties. To obtain these optimum performances, single component coatings are not suitable. There is a need to have two components system. In this present work, epoxy and polyester resins were selected due to their advantages over different functional properties. Polyester resin was purchased from Bayer Material Science and the type of polyester code is (RD 181X) as in Appendix B. Meanwhile, the epoxy resin was purchased from Nan Ya Plastics Corporation. The samples were depicted in Figure 3.2. Both of the resins were mixed and xylene was used as solvent. These coating systems were then mixed with polyisocyanate (NCO) that acted as hardener. The amount of NCO can be calculated by the given equation:

$$\frac{2.47 \times \%OH \text{ of polyester}}{\%NCO} \times \text{mass of polyester used} \dots\dots \text{Equation 5}$$

where mass of polyester is in gram (g) unit. (Huybrechts and Tanghe, 2007).

Different hybrid coating systems were prepared by varying the weight percentage of polyester and epoxy resin ratios as presented in Table 3.1.

Table 3.1: Compositions of polyester-epoxy in binder coating systems

| Sample | Designation | Polyester(wt. %) | Epoxy(wt. %) |
|--------|-------------|------------------|--------------|
| A1 | 100P | 100 | 0 |
| A2 | 90P10E | 90 | 10 |
| A3 | 80P20E | 80 | 20 |
| A4 | 70P30E | 70 | 30 |
| A5 | 60P40E | 60 | 40 |
| A6 | 50P50E | 50 | 50 |

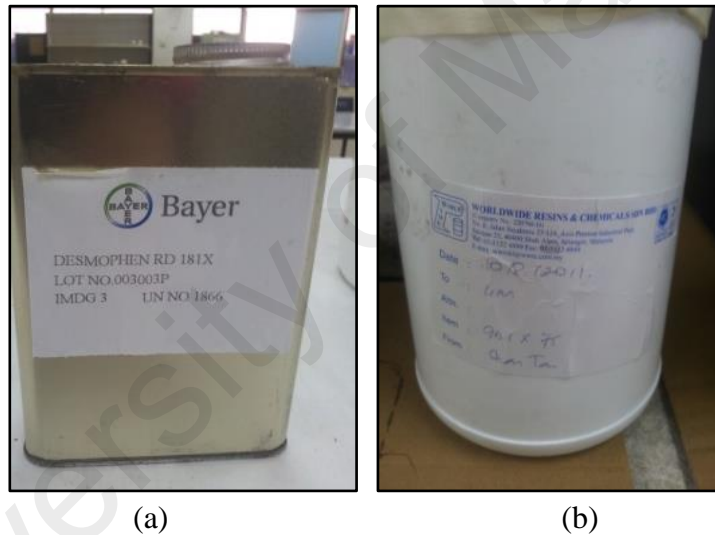


Figure 3.2: Polymers (binders) used (a) polyester resin (b) epoxy resin

3.1.2 Biocide system

The best performing binder composition was chosen to develop antifouling coating system. In this work, copper and copper oxide were purchased from Sigma-Aldrich. Different pigment volume concentrations (PVC) up to 25% was added with the binder system. PVC can be calculated by the following equation:

$$PVC = \frac{\text{volume of pigment}}{\text{volume of pigment} + \text{volume of binder}} \times 100 \% \dots \dots \text{Equation 6}$$



Figure 3.3: Pictures of (a) copper and (b) copper oxide powder purchased from Sigma-Aldrich

The density of copper and copper oxide is 8.94g/mL and 6.32g/mL respectively. The amounts of copper and copper oxide added with respect to the PVC values are tabulated in Table 3.2 and Table 3.3.

Table 3.2: Compositions of copper biocides system

| Sample | PVC % | Amount of binder (g) | Amount of copper (g) |
|--------|-------|----------------------|----------------------|
| B1 | 5 | 20.00 | 8.699 |
| B2 | 10 | 20.00 | 18.364 |
| B3 | 15 | 20.00 | 29.165 |
| B4 | 20 | 20.00 | 41.320 |
| B5 | 25 | 20.00 | 55.097 |

Table 3.3: Compositions of copper oxide biocides system

| Sample | PVC % | Amount of binder (g) | Amount of copper oxide (g) |
|--------|-------|----------------------|----------------------------|
| C1 | 5 | 20.00 | 6.150 |
| C2 | 10 | 20.00 | 12.982 |
| C3 | 15 | 20.00 | 20.618 |
| C4 | 20 | 20.00 | 29.213 |
| C5 | 25 | 20.00 | 38.950 |

The addition of copper and copper oxide was varied up to 25 % of pigment volume concentration for both systems. This is because the solution has saturated.

3.1.3 Booster biocides system

To enhance the performance of the develop antifouling coating system, there is an attempt to add booster biocides. The highest coating resistance was found to be at 25% PVC for both biocides system. Different percentage of diuron that acts as booster biocides was added in the antifouling coating system. Again, the coating resistance was determined in the characterization part. The compositions of diuron booster biocides system is tabulated in Table 3.4.

Table 3.4: Compositions of diuron in copper oxide biocides system

| Sample | Diuron % | Amount of binder (g) | Amount of copper oxide (g) | Amount of diuron (g) |
|--------|----------|----------------------|----------------------------|----------------------|
| E1 | 1 | 20.00 | 38.950 | 0.595 |
| E2 | 3 | 20.00 | 38.950 | 1.823 |
| E3 | 5 | 20.00 | 38.950 | 3.102 |

3.2 Application of coatings on mild steel panels

Cod rolled mild steel panels were used for coating application. For better coating performance, surface preparation plays an important role. First, the metal plates were cleaned in organic solvent (thinner) to remove the grease and dirt. Metal plates were sand blasted using grit to achieve standard metal surface. The binder systems were applied by brush method on the metal substrate. The coated panels were left to cure in room temperature for a week before they were tested for their property analyses. The thicknesses of the samples were then measured by using a coating thickness gauge from Elcometer. Dry film thicknesses were found to be at $50 \pm 5\mu\text{m}$ after completely cured. Figure 3.4 shows some pictures of the substrates.

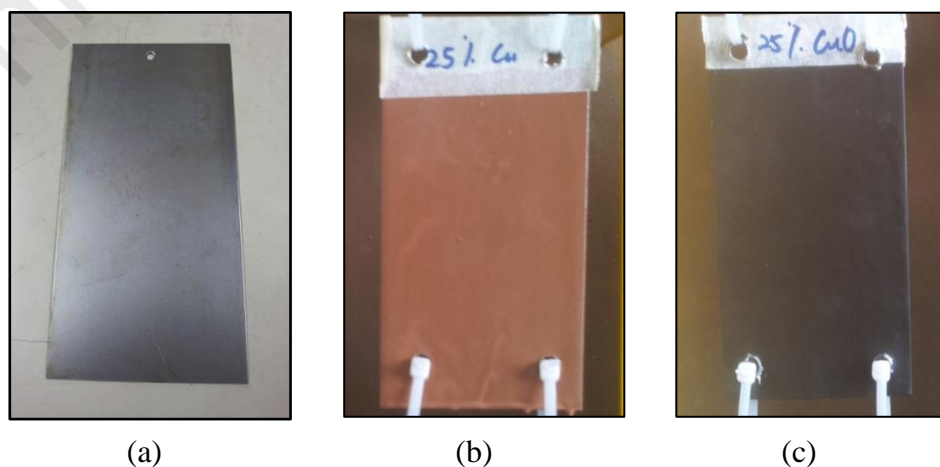


Figure 3.4: Pictures of (a) steel panels used and (b) and (c) copper oxide coated panels after being cured

3.3 Performance of Binder (Structural & Adhesion Power)

3.3.1 Differential scanning calorimetry (DSC)

Thermal studies were carried out using differential scanning calorimetry (DSC). This technique permits one to investigate physical changes in the material while heating. The glass transition, T_g occurs when material changes from glassy to a rubbery state (Parra *et al.*, (2002). In the present work, the DSC was performed using DSC Q200 analyzer (TA, USA). Analysis of the DSC curves gives the glass transition temperature, T_g . The samples were sealed in standard aluminium crucibles and cooled in a nitrogen atmosphere at $-50\text{ }^\circ\text{C}$. The samples were then heated at the rate of $10\text{ }^\circ\text{C}/\text{min}$. up to $250\text{ }^\circ\text{C}$ and then cooled down to $-50\text{ }^\circ\text{C}$ again. This heating-cooling-heating cycle was done for three cycles.

3.3.2 Fourier Transform-Infrared Spectroscopy (FTIR)

FTIR can be used for the identifications of functional groups and determination of cross-linking between the reactants. The FTIR spectra were recorded in the transmittance mode using ATR-Nicolet iS10 Spectrometer (Thermo Fisher Scientific Inc.). The spectra were recorded after a 32-scan data accumulation in the range of $400\text{--}4000\text{ cm}^{-1}$ at a spectral resolution of 4.0 cm^{-1} .

3.3.3 Pull off adhesion test

The evaluation of mechanical properties of the coating is very important since these will be applied on metal substrate and for outdoor applications. Adhesion is very much necessary for the longer lifetime of coatings. The pull off adhesion test was carried out to determine the adhesion power of the binder coating system to the mild steel substrate. Pull off Adhesion Tester model Elcometer 106/2 was used in this study. A test dolly is

bonded to the coating using an adhesive. The dolly is pulled off the surface and the force required to remove the dolly was obtained from the scale indicator. Pictures after the pull off test were then captured to analyse the coating adhesion.

3.4 Coating Resistance Measurement

Electrical impedance spectroscopy (EIS) measurement has been used to determine the coating resistance and to the best coating performance of organic coatings. In this EIS measurement, the electrode system such as Ag/AgCl reference electrode, platinum counter electrode and the mild steel panel as the working electrode was employed. The coated mild steel panel was exposed to a known area with the artificial seawater. A cylindrical plastic tube was mounted on the coated surface. The experimental setup for this measurement is illustrated in Figure 3.5 below:

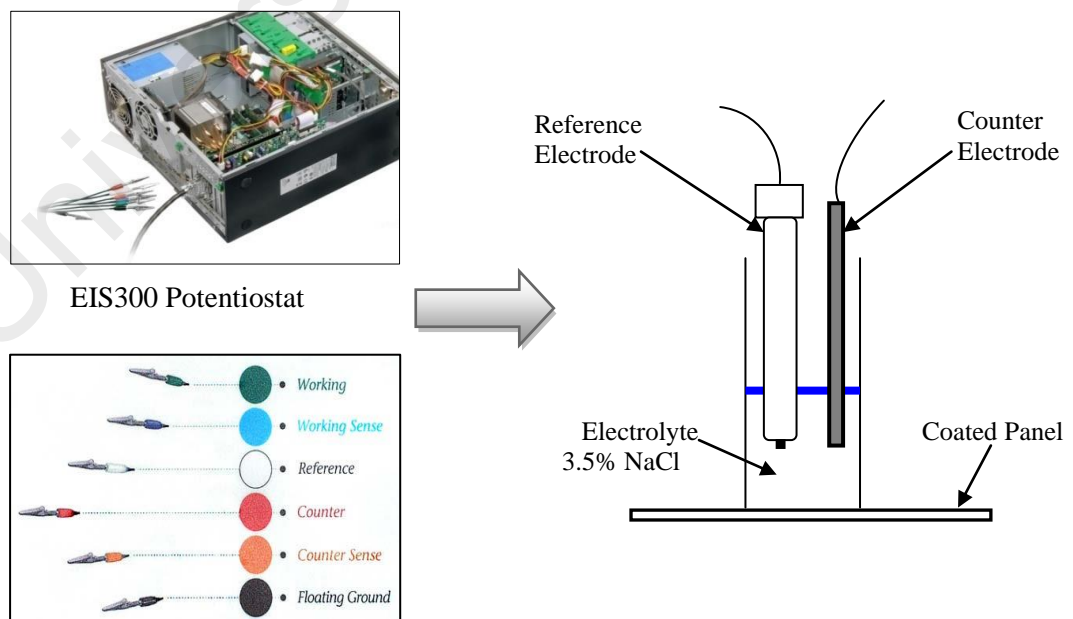


Figure 3.5: Experimental setup for EIS measurement

The EIS measurements were carried out with EIS300 potentiostat from Gamry and the data collected from the software were analyzed by modelling the data on known equivalent circuits which is a standard tool for the interpretation of impedance data using the Bode plot. The measurement was done for 30 days and the coating resistance value, R_c was calculated by analyzing Bode plots in the frequency range from 0.01 to 300 kHz at room temperature. The coating resistance value obtained from all compositions has been used to determine the best coating resistance behavior for all coating systems prepared. Figure 3.6 is the sample Bode plot for coating resistance calculation obtained from the Gamry Echem Analyst software

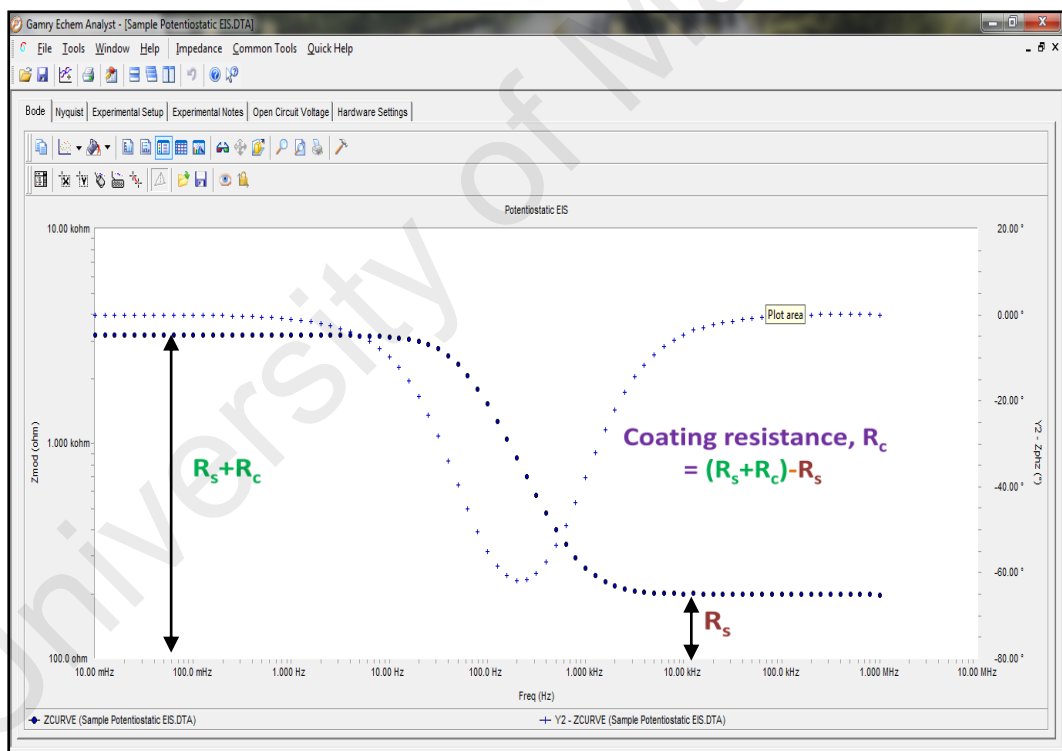


Figure 3.6: Bode plot to obtain coating resistance, R_c

3.5 Metal Leaching Concentration

Inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of trace metals in a solution. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. It is a flame technique with a flame temperature in a range from 6000 to 10000 K. The plasma excites atoms, which leads to photon emission and ionization. It has a high stability and considered as inert environment and low interference and this makes the ICP-OES produce better qualitative and quantitative analytical data. The emitted radiation from the plasma is then used for analysis. Figure below shows the diagram of ICP-OES sample characterization.

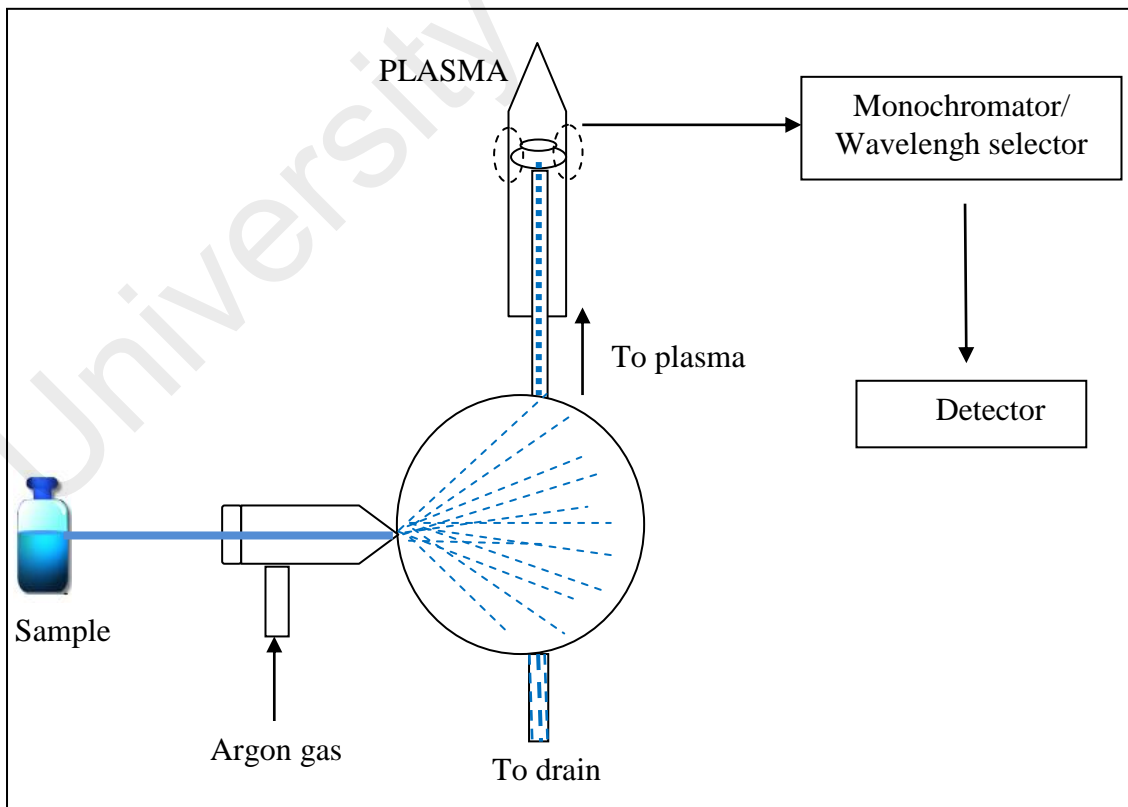


Figure 3.7: Diagram of sample introduction to ICP-OES

For the sample characterization, the coated panels were put in an individual beaker and immersed in different solutions such as distilled water, artificial seawater (3.5% sodium chloride), and real seawater. The beakers were then placed in water bath incubator shaker to create a continuous simulated wave motion in room temperature. About 7 mL solutions from the each beaker were taken for every 10 days to run the Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES) test to obtain the metal leaching or metal concentration for the highest coating resistance samples for biocides systems



Figure 3.8: Metal leaching concentration determination from ICP/OES

3.6 Real Exposure in Seawater

The selected coated panels were exposed in a seawater environment in Malacca Straits, Malaysia where the marine activity was held. Two places have been chosen to carry out this test to see the difference of seawater environment on the coated steel plates. The locations are in Perak and Penang area. Figure 3.9 shows the map of the location stated.



Figure 3.9: Location on map for the seawater exposure (circled area)

The coated mild steel panels and glass coated samples were hanged with custom made cages to let the coated panels exposed directly to the seawater environment. The pictures were taken before and after immersion for every 10 days for 30 days to see the physical changes of the coated panel surface. It is to be noted that the coated panels were rinse and wiped with a soft wet sponge before the pictures were taken.

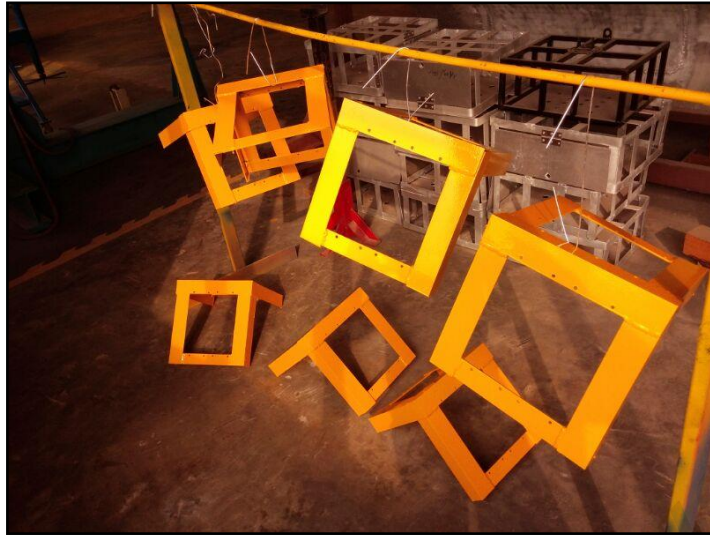


Figure 3.10: Custom made cages to hang the steel panels

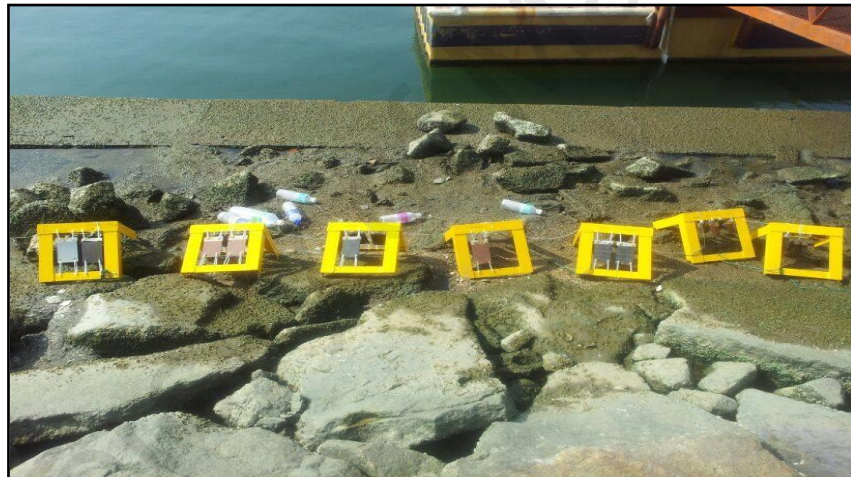


Figure 3.11: Coated panels before immersion in seawater



Figure 3.12: Coated panels after immersion in seawater

3.7 Glossiness Test

Glossmeter is an instrument which can be used to measure gloss intensity of a surface. Gloss is determined by projecting a light beam at a fixed intensity and angle onto a surface and amount of reflected light is measured at an equal but opposite angle. The ratio of reflected to incident light compared to the ratio for the gloss standard, is known as gloss units (GU). The measurement angles are specified to cover the majority of industrial coating application. Selection of reading angle is based on the gloss range as shown in Table 3.5 below:

Table 3.5: Gloss angle based on gloss range of a coated surface

| Gloss Range | 60° Value | Remarks |
|--------------------|------------------|---|
| High Gloss | >70 GU | If measurement exceeds 70 GU, change test setup to 20° |
| Medium Gloss | 10 - 70 GU | |
| Low Gloss | <10 GU | If measurement is less than 10 GU, change test setup to 85° |

In this work, the glossiness of the coated surface was determined using glossmeter which was purchased from KSJ with model MG268-F2 Multi Angle Gloss Meter: 20, 60, 85°. The glossmeter is designed and manufactured following the standard ISO 2813.



Figure 3.13: Glossmeter

The glossiness test was carried out for the samples before and after immersion under seawater for 30 days. Figure 3.13 represents the glossmeter used in this research project. The reading was taken at least three times and the average value was then determined.

3.8 Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) was carried out for both coating systems which were applied on a glass slide to see the microscopic changes to the coating surface before and after immersion in seawater. The samples were hanging with custom made cages to let the coated samples exposed directly to the seawater. The TM3030 tabletop microscope from Hitachi High-Technologies Europe (Germany) was used to study the surface morphology of the exposed area for the samples collected from the field test with the same magnification of 500x and 5kV of accelerating voltage.



Figure 3.14: Scanning Electron Microscope (SEM)

CHAPTER 4: RESULTS ON COATING RESISTANCE

4.0 Introduction

A property of a coating that can be used to determine how good it performs against corrosion is the coating resistance. The corrosion performance of organic coatings has been widely researched using electrochemical impedance spectroscopy (EIS). Data collected via impedance techniques can be analyzed by modelling the data on known equivalent circuits which is a standard tool for the interpretation of impedance data using the Bode plot (Bonora *et al.*, 1996; McIntyre and Pham, 1996; Hinderliter *et al.*, 2006; Amirudin and Thierry, 1995; Grundmeier *et al.*, 2000; Dhoke and Khanna, 2012). The data were collected for a period of 30 days exposing the coatings in 3.5% sodium chloride (NaCl) solution which can be considered as simulated seawater (Deflorian *et al.*, 1998; Olad and Nosrati, 2012; Naderi *et al.*, 2004; Hu *et al.*, 2003; Ananda Kumar and Sasikumar, 2010). The coating resistance value was calculated by analyzing Bode plots in the frequency range from 0.01 Hz to 300 kHz at room temperature. The variation in the coating parameters have been used to determine the best corrosion resistance behavior of the coating system.

4.1 Coating Resistance for Polyester-Epoxy Binder System

Different compositions of polyester-epoxy binder systems have been prepared by varying the polyester content from 50 to 100 wt. %. From EIS, the Bode plot has been established to evaluate the coating resistance, R_c for the polyester/epoxy binder system for 30 days of immersion in the artificial seawater. Figure 4.1 shows the examples of Bode plots obtained for the polyester-epoxy binder system.

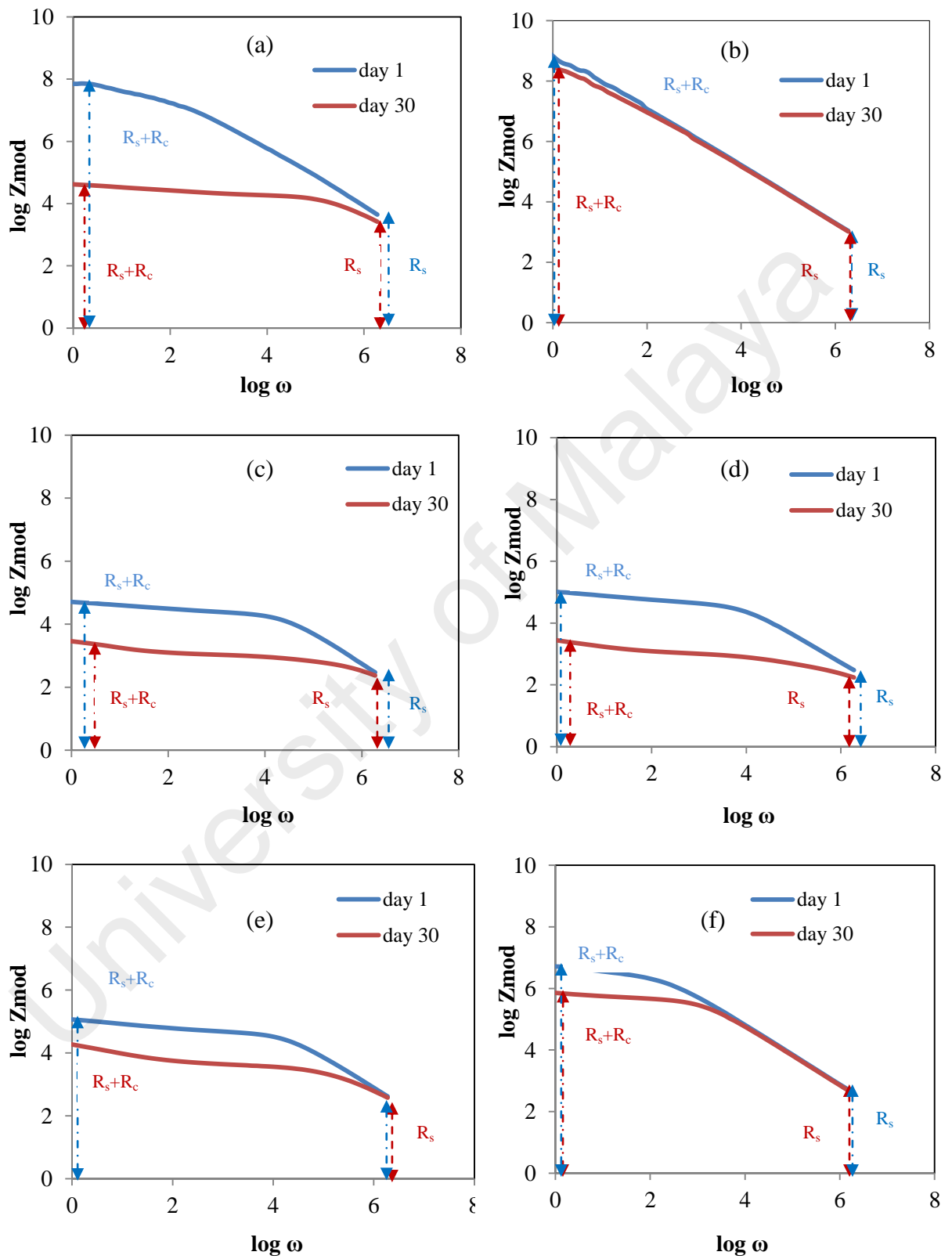


Figure 4.1: Bode plots for polyester-epoxy binder system; (a) 100% polyester, (b) 90% polyester, (c) 80% polyester, (d) 70% polyester, (e) 60% polyester and (f) 50% polyester

The value of coating resistance R_c was then plotted versus time (days) as shown in Figure 4.2 and the calculated values for each samples are tabulated in Table 4.1.

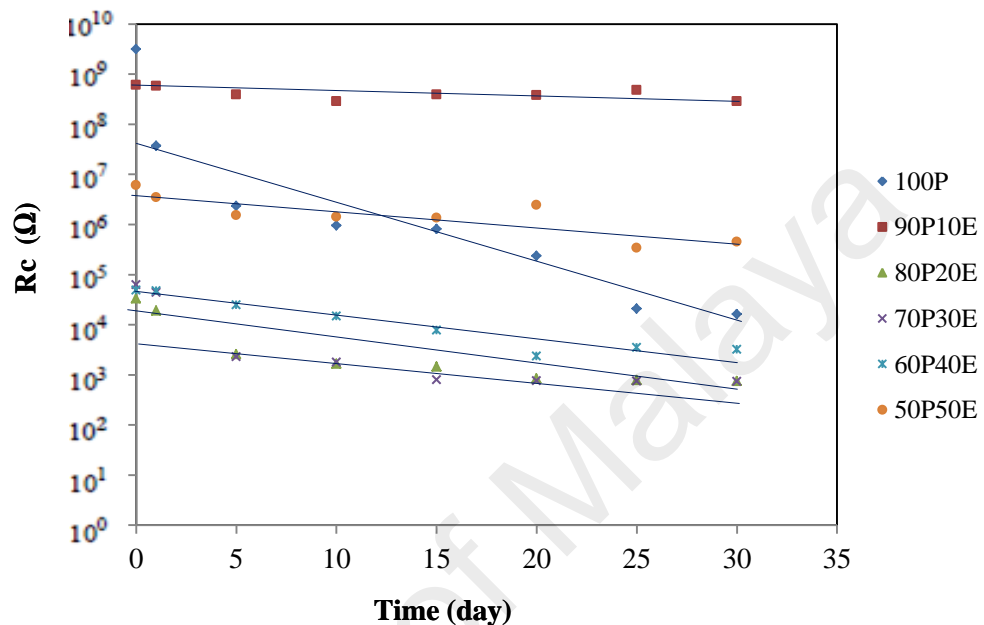


Figure 4.2: Coating resistance (R_c) of polyester (P)/epoxy (E) coating system for 30 days of immersion in 3.5% NaCl

From Figure 4.2, coating resistance, R_c shows decreasing value with increasing immersion time in 3.5% artificial seawater. The analysis from the Bode plot shows that the composition of 90 wt. % of polyester gives the best corrosion resistance value. The coating resistance of the sample was found to be in the range of 10^8 ohm throughout the time of exposure. At the end of 30 days of exposure, the R_c value was found to be 2.89×10^8 ohm. The binder system of 50P50E consisting equal amounts of polyester and epoxy has also shown good protection capabilities since the coating system had coating resistance higher than 10^6 ohm up to 30 days of immersion (Amirudin and Thierry, 1995). The coating resistance of the other blended samples was already low (less than $10^5 \Omega$) since beginning and decreased with increasing immersion time (30 days) with coating resistance below the 10^5 ohm. Table 4.1 shows the compositions of the

polyester/epoxy resins and the coating resistance values obtained during the 30days of immersion in 3.5% of NaCl solutions.

Table 4.1: The values of coating resistance, R_c with different composition of polyester

| Sample | Weight percentage (wt. %) of polyester: epoxy | Coating Resistance, $R_c(\Omega)$ @ day 1 | Coating Resistance, $R_c(\Omega)$ @ day 30 | *Approximate Rate of decrease of R_c (Ω /day) |
|--------|---|---|--|---|
| A1 | 50:50 | 3.5×10^6 | 4.5×10^5 | -1.3×10^4 |
| A2 | 60:40 | 4.8×10^4 | 3.2×10^3 | -1.5×10^3 |
| A3 | 70:30 | 4.4×10^4 | 7.5×10^2 | -7.7×10^2 |
| A4 | 80:20 | 1.9×10^4 | 7.6×10^2 | -1.5×10^3 |
| A5 | 90:10 | 5.9×10^8 | 2.9×10^8 | -9.0×10^6 |
| A6 | 100:0 | 3.7×10^4 | 1.6×10^4 | -8.3×10^4 |

*Rate of decrease of coating resistance is assumed linear in this work

4.2 Coating Resistance for Biocides Coating System

4.2.1: Coating Resistance for Copper based Coating System

The coating resistance for different pigment volume concentrations (PVC) of copper based coating system was analysed using electrical impedance spectroscopy (EIS). The copper percentage was varied ranging from 0 to 25% of PVC. The compositions of copper content in the coating system were varied according to the equation below:

$$\% \text{ PVC of copper} = \frac{\text{volume of pigment (Cu)}}{\text{volume of pigment (Cu)+volume of binder}} \times 100 \% \dots \text{Equation 7}$$

As mentioned in Chapter 3, the best binder composition which is 90% polyester and 10% epoxy blended resin has been used as binder. Figure 4.3 shows the Bode plots obtained for day 1 and day 30 for copper based biocide coating system.

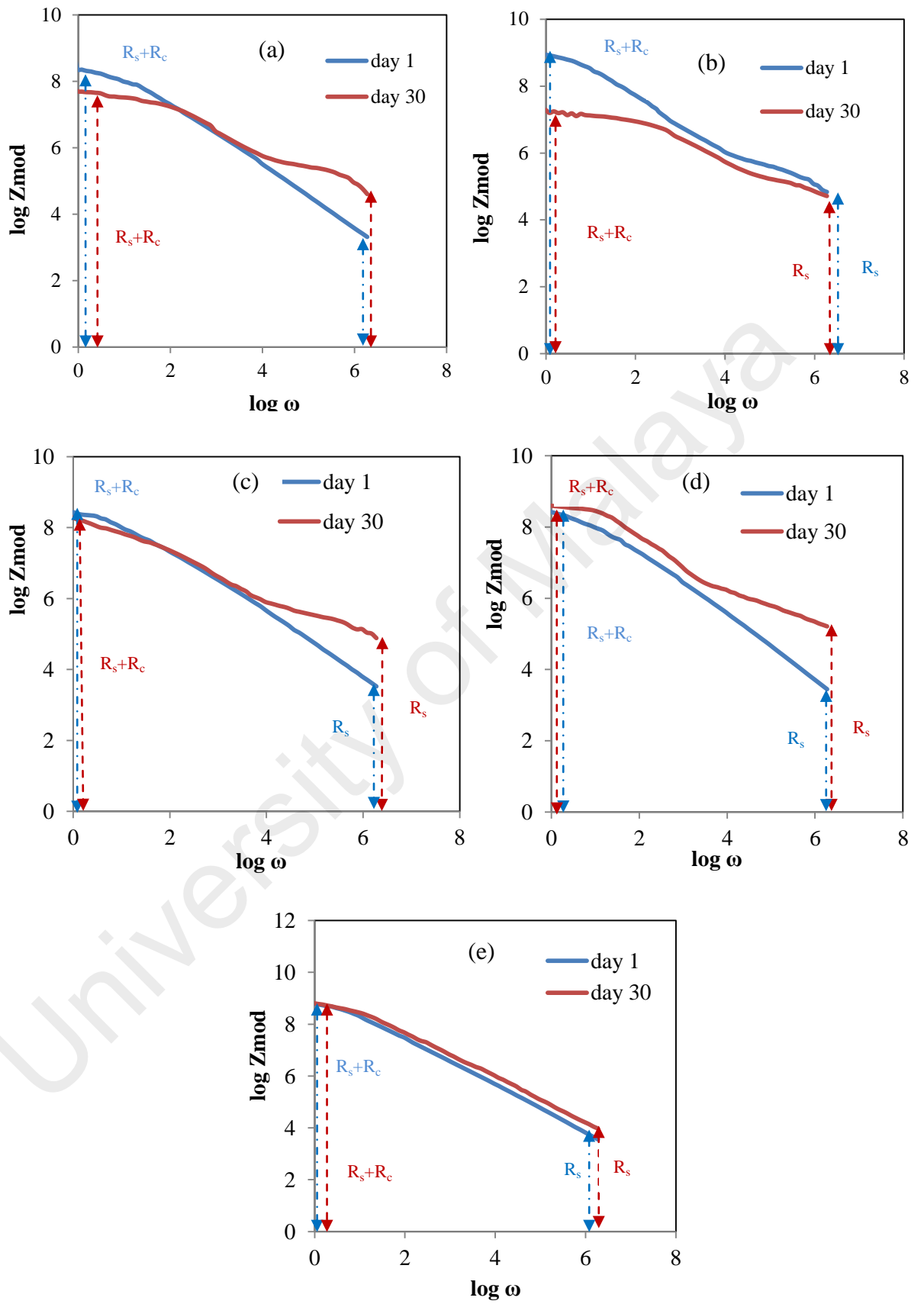


Figure 4.3: Bode plots for copper based biocides coating system at day 1 and day 30; (a) 5% PVC, (b) 10% PVC, (c) 15% PVC, (d) 20% PVC, (e) 25% PVC

From the Bode plots, the values of coating resistance can be calculated. Figure 4.4 shows the variation of coating resistance with different composition of copper content from day 0 to day 30.

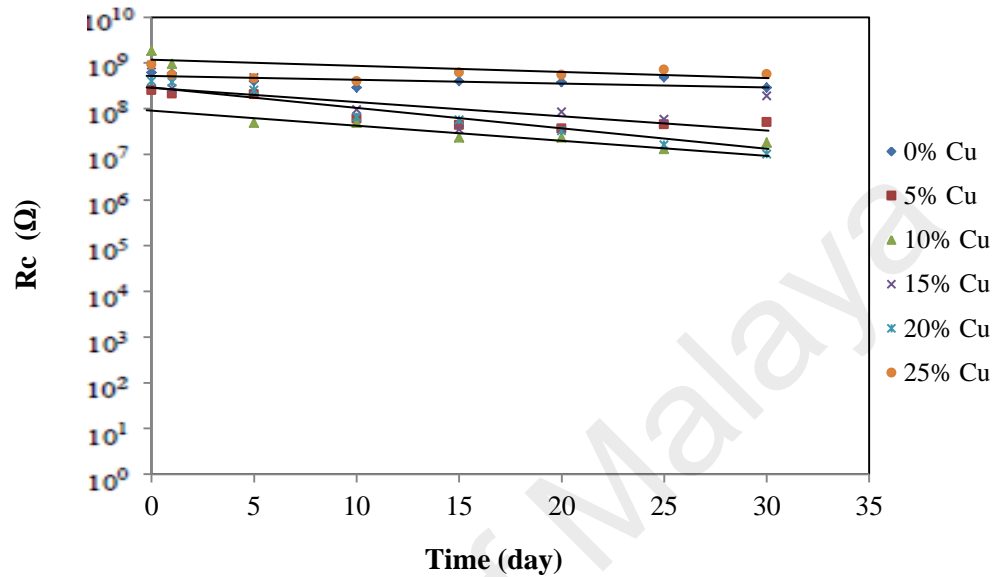


Figure 4.4: Coating resistance (R_c) of copper based coating system for 30 days of immersion in 3.5% NaCl.

Figure 4.4 shows the decreasing value of coating resistance, R_c with increasing time of immersion. The highest coating resistance was obtained for the sample with 25% PVC of copper which gives the value of 5.7×10^8 ohm. Table 4.2 shows the composition of copper based coating system and the obtained values of coating resistance towards the end of exposure in artificial seawater.

Table 4.2: The values of coating resistance, R_c with different pigment volume concentration (PVC) of copper.

| Sample | Pigment Volume Concentration (PVC %) | Coating Resistance, R_c (Ω) @ day 1 | Coating Resistance, R_c (Ω) @ day 30 | *Approximate Rate of decrease of R_c (Ω /day) |
|--------|--------------------------------------|--|---|---|
| B1 | 5 | 2.1×10^8 | 5.0×10^7 | -7.0×10^6 |
| B2 | 10 | 9.5×10^8 | 1.8×10^7 | -4.0×10^7 |
| B3 | 15 | 2.7×10^8 | 1.9×10^7 | -2.0×10^7 |
| B4 | 20 | 3.8×10^7 | 1.0×10^7 | -1.0×10^7 |
| B5 | 25 | 5.5×10^8 | 5.7×10^8 | -1.0×10^6 |

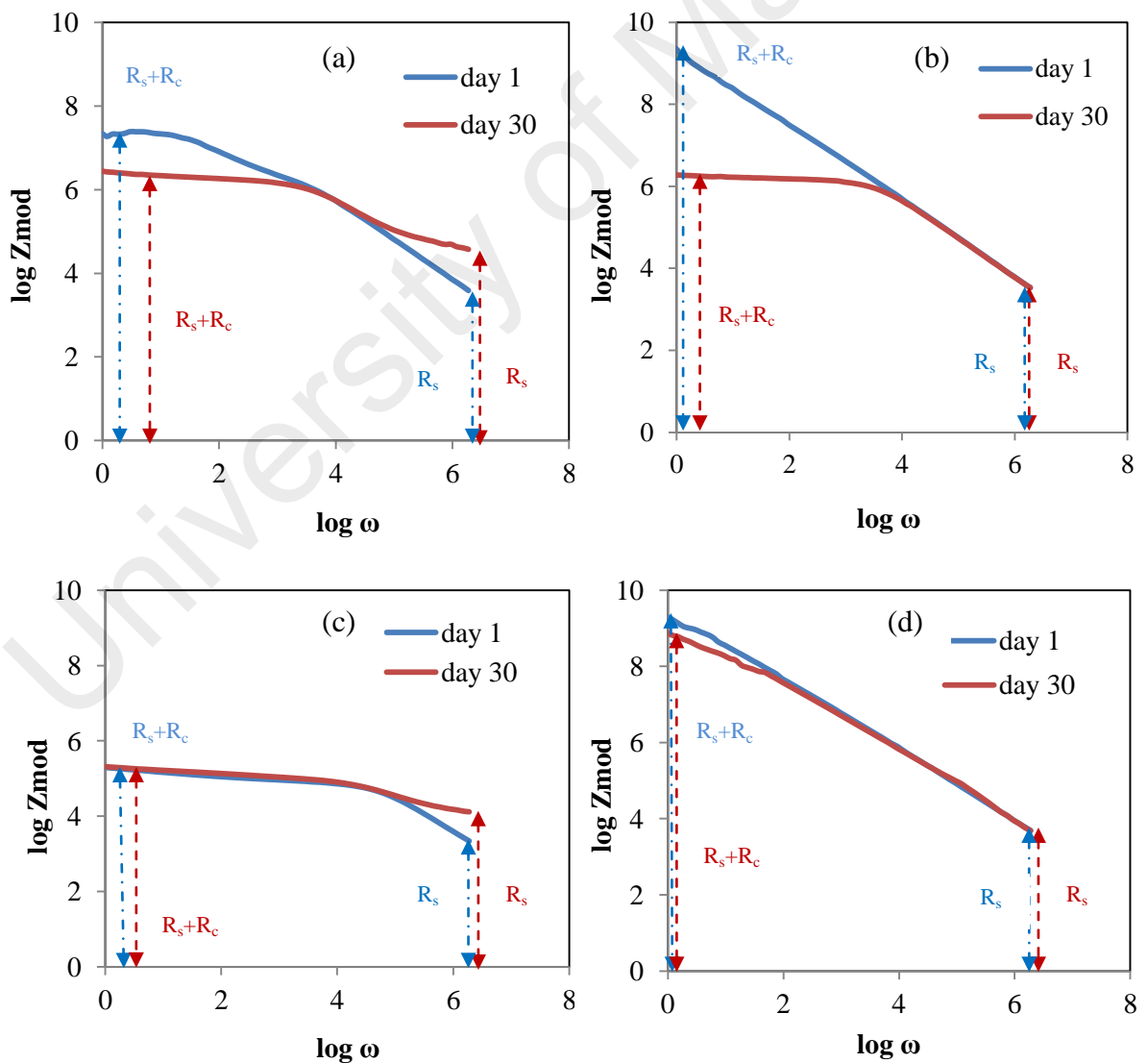
*Rate of decrease of coating resistance is assumed linear in this work.

4.2.2 Coating Resistance for Copper Oxide based Coating System

The copper oxide percentage was varied ranging from 0 to 25% of PVC. The compositions of copper content in the coating system were varied according to the equation below:

$$\% \text{ PVC of copper oxide} = \frac{\text{volume of pigment (CuO)}}{\text{volume of pigment (CuO)+volume of binder}} \times 100 \dots \text{Equation 8}$$

Figure 4.5 shows the Bode plots for day 1 and day 30 for copper oxide biocide coating system.



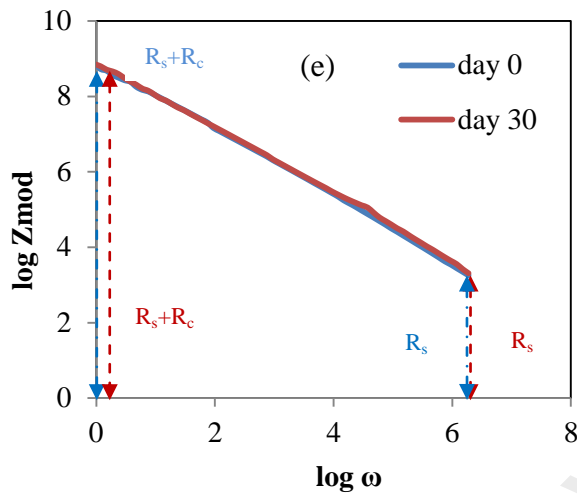


Figure 4.5: Bode plots for copper oxide based biocides coating system at day 1 and day 30; (a) 5%PVC, (b)10% PVC, (c) 15% PVC, (d) 20% PVC, (e) 25% PVC

Figure 4.6 shows the plot of coating resistance with the immersion time in artificial seawater for 30 days.

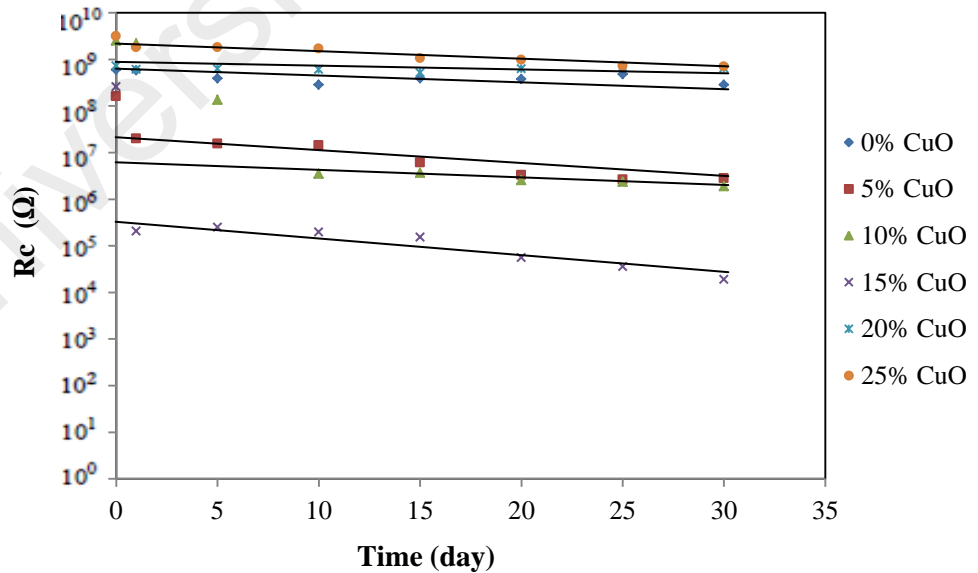


Figure 4.6: Coating resistance (R_c) of copper oxide based coating system for 30 days of immersion in 3.5% NaCl

Based on the results shown in Figure 4.6, it can be observed that the coating resistance is decreased with increasing time of exposure in artificial seawater. Like in the copper based coating system before, the highest value of coating resistance, R_c at the end of exposure is observed for the sample with 25% PVC of copper oxide content. Referring to Figure 4.5 (e), the result showed that the Bode plot for the sample is almost similar at the early and at the end of exposure in artificial seawater. This showed that the solution resistance, R_s and the pore resistance, R_c of the coated panels was not affected by the electrolyte. Hence, this composition gave the best corrosion protection for the copper oxide coating system. The R_c value obtained for the sample is at 7.1×10^8 ohm. Table 4.3 below shows the coating resistance value at the end of exposure for each sample.

Table 4.3: The values of coating resistance, R_c with different pigment volume concentration (PVC) of copper oxide

| Sample | Pigment Volume Concentration (PVC %) | Coating Resistance, $R_c(\Omega)$ @ day 1 | Coating Resistance, $R_c(\Omega)$ @ day 30 | *Approximate Rate of decrease of R_c (Ω /day) |
|--------|--------------------------------------|---|--|---|
| C1 | 5 | 2.016×10^7 | 2.839×10^6 | -3.0×10^6 |
| C2 | 10 | 2.219×10^9 | 1.919×10^6 | -7.0×10^7 |
| C3 | 15 | 2.101×10^5 | 1.933×10^4 | -4.0×10^6 |
| C4 | 20 | 6.136×10^8 | 6.603×10^8 | -2.3×10^4 |
| C5 | 25 | 1.846×10^9 | 7.107×10^8 | -7.0×10^7 |

*Rate of decrease of coating resistance is assumed linear in this work.

CHAPTER 5: RESULTS ON METAL LEACHING CONCENTRATION

5.0 Introduction

Biocide based antifouling coatings have been designed to prevent corrosion and biofouling. In marine application, biocidal coatings are used to kill microorganism and fungi in the seawater by releasing slowly the biocide from the coating film into the seawater. Seawater contains more dissolved ions than freshwater such as sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), strontium (Sr^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), bromide (Br^-), borate (H_3BO_4^-) and fluoride (F^-). Depending on the solubility of the biocides in seawater, an appropriate leaching rate of the released biocides is one of the important characteristics in preventing fouling (Woods Hole Oceanographic Institution, WHOI 1952; Yebra *et al.*, 2004; Chambers *et al.*, 2006; Chen *et al.*, 2013; Schiff *et al.*, 2004; Oikonomou *et al.*, 2012). The leaching rate of biocides should not be too fast that can cause in rapid depletion of antifouling characteristics and unnecessarily high concentration in the sea. However, if the release rate is too slow, which is too insoluble, it will not dissolve sufficiently to prevent fouling (Rathish *et al.*, 2013).

The elemental analysis of copper and copper oxide based biocides antifouling coatings was carried out using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). It is an analytical technique used to detect the traced metals using inductively coupled plasma. It is a type of emission spectroscopy that produced excited atoms and ions that emit electromagnetic radiation at certain wavelengths characteristic of a particular element.

In this work, copper and copper oxide based coated panels (coated area of 63cm²) with the highest pigment volume concentration were immersed in 200 mL of different solutions such as distilled water, artificial seawater (3.5% sodium chloride), and real seawater to study the leaching concentration of the biocides added in the coating's formulations. Leaching rate of both biocides can be calculated using Equation 9 below: (Kojima *et al.*, 2014; Woods Hole Oceanographic Institution, 1952)

$$\text{Leaching Rate (mg /cm}^2\text{)} = \text{CAF} \times \text{V} \times 24\text{h} / (\text{A} \times \text{T}) \quad \dots \text{Equation 9}$$

where,

CAF= concentration of antifoulant agent (mg/L)

V= volume of electrolyte

A= exposed area of paint surface

T = sampling period of time

5.1 Metal Leaching Concentration for Copper based Coating System

The coated sample with 25 % PVC of copper was chosen to investigate the metal leaching concentration from the coating system. Table 5.1 and Figure 5.1 show the copper concentration in three types of electrolytes as below:

Table 5.1: Values of metal leaching concentration in mg/L in different type of electrolytes

| Day | Distilled water | Artificial seawater | Seawater | Leaching rate in seawater (mg/cm ² /day) |
|-----|----------------------------|---------------------|----------|---|
| | Metal concentration (mg/L) | | | |
| 5 | <0.01 | 0.09 | 32.59 | 0.021 |
| 10 | 0.05 | 0.18 | 37.04 | 0.012 |
| 20 | 0.45 | 2.49 | 53.67 | 8.519 |
| 30 | 0.85 | 8.46 | 140.80 | 14.899 |

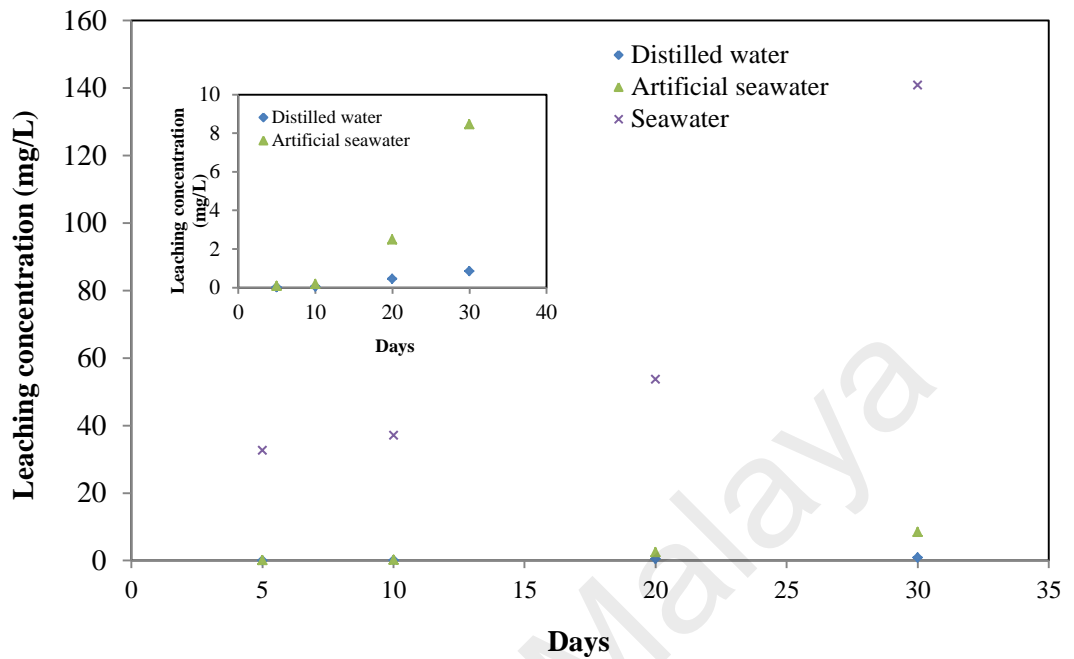


Figure 5.1: Leaching concentration of copper (mg/L) in different types of electrolyte

Based on the results obtained, we can see that the variation of copper leaching concentration in copper based biocides coating system gives obvious difference in different types of electrolytes. The highest concentration was found in seawater which is at 140.80 mg/L at day 30 whereas the least copper concentration is observed for the sample placed in distilled water. The copper concentration in artificial seawater is approximately 10 times of the concentration in distilled water at the end of the experiment. This may be due to more dissolved ions available in seawater than freshwater that increases the chemical reaction as shown in Equation 4. For example, chloride ion is derived from sodium chloride which is the main compound in the seawater composition that led to the corrosion initiation.

5.2 Metal Leaching Concentration for Copper Oxide based Coating System

For the copper oxide coating system, the sample with 25 % PVC of copper oxide was used to study the leaching concentration of copper oxide from the coating system. Table 5.2 and Figure 5.2 below show the results of copper oxide concentration in three different electrolytes.

Table 5.2: Values of metal leaching concentration in mg/L in different type of electrolytes

| Day | Distilled water | Artificial seawater | Seawater | Leaching rate in seawater (mg/cm ² /day) |
|-----|----------------------------|---------------------|----------|---|
| | Metal concentration (mg/L) | | | |
| 5 | <0.01 | 0.11 | 40.80 | 0.026 |
| 10 | 0.06 | 0.23 | 46.36 | 14.717 |
| 20 | 0.56 | 8.12 | 67.19 | 10.665 |
| 30 | 1.06 | 10.85 | 176.26 | 18.652 |

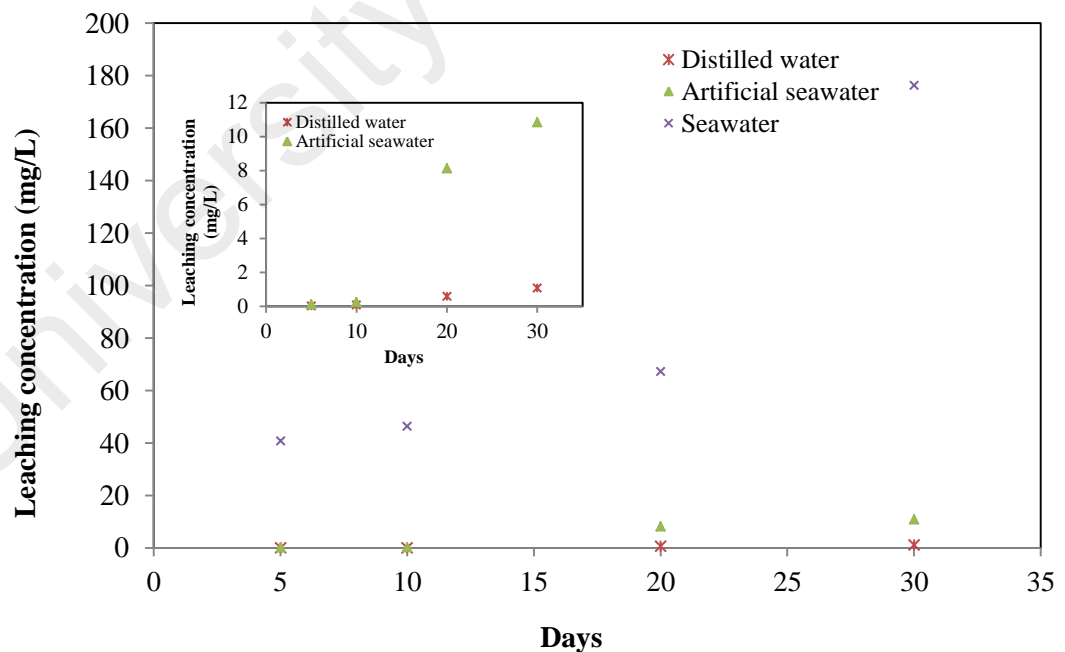


Figure 5.2: Leaching concentration of copper oxide (mg/L) in different type of electrolytes

Referring to the results presented in Table 5.2 and Figure 5.2, the copper oxide leaching concentration in the coating system also shows obvious value difference in each electrolyte. As in previous system, the highest concentration was found in seawater electrolyte which is at 176.26 mg/L which is higher than the concentration found in the copper coating system. The increase of copper oxide concentration in artificial seawater is also approximately 10 times of the copper oxide concentration in distilled water. As expected, the least copper oxide concentration was also observed for the sample placed in distilled water at day 30.

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CHAPTER 6: RESULTS ON REAL EXPOSURE TO SEAWATER

6.0 Introduction

In an attempt to enhance the antifouling property, the biocide coating system has been added with diuron as booster biocides. The visual observation shows that the addition of diuron coated panel enhances glossiness of the coating. In real situation, copper oxide coating system seems to be the better biocide. So, it would be beneficial to study the real situation in seawater of copper oxide and copper oxide-diuron based antifouling coatings. In this case, the copper based coating system is less appealing for use in preventing marine fouling. The field test exposure in seawater environment has been reported by (Kharchenko *et al.*, 2012; Olsen *et al.*, 2010; Oikonomou *et al.*, 2012) to study the real situation of the coatings. According to the report by Woods Hole Oceanographic Institution (WHOI 1952), biofouling depends on numbers of parameters. The water condition, geographical location and types of operating vessels might give different biofouling effects.

In this work, the real performance of the developed copper oxide and copper oxide-diuron antifouling coating systems have been tested by exposing the coated panels for 30 days in seawater. The locations of the field test conducted were at Lumut in the state of Perak and along the coast at Pulau Betong in Penang Island. Both states are on the west coast of Peninsular Malaysia where there are many marine activities. The samples were hanged in seawater 2 meter away from the seashore. The panels were analysed to check the effect and growth of microorganisms. The surface was washed and photographs taken at 10 days interval.

6.1 Physical Effects for Polyester-Epoxy Binder System

The best performing binder (90P:10E) coated plates were exposed in seawater to evaluate their antifouling property. Figure 6.1 and Figure 6.2 below show the physical effects for every 10 days of immersion in seawater in Lumut and Penang Island, respectively.

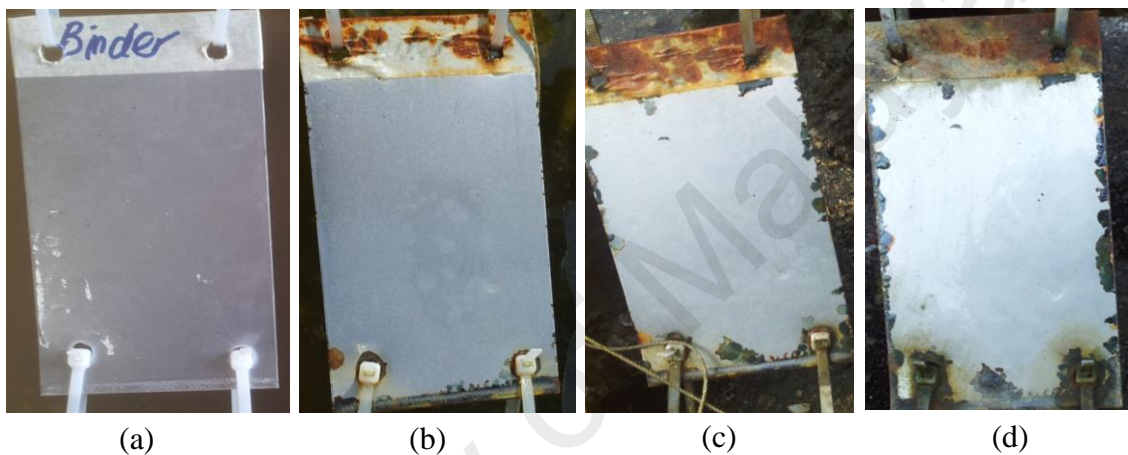


Figure 6.1: Exposure of polyester-epoxy binder coating in seawater for 30 days: (a) day 0, (b) day 10, (c) day 20, (d) day 30 in Lumut, Perak

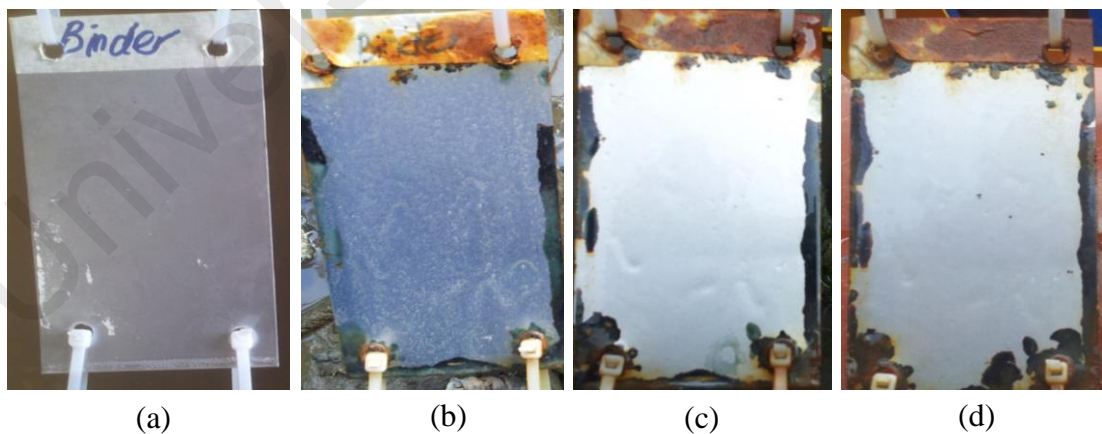
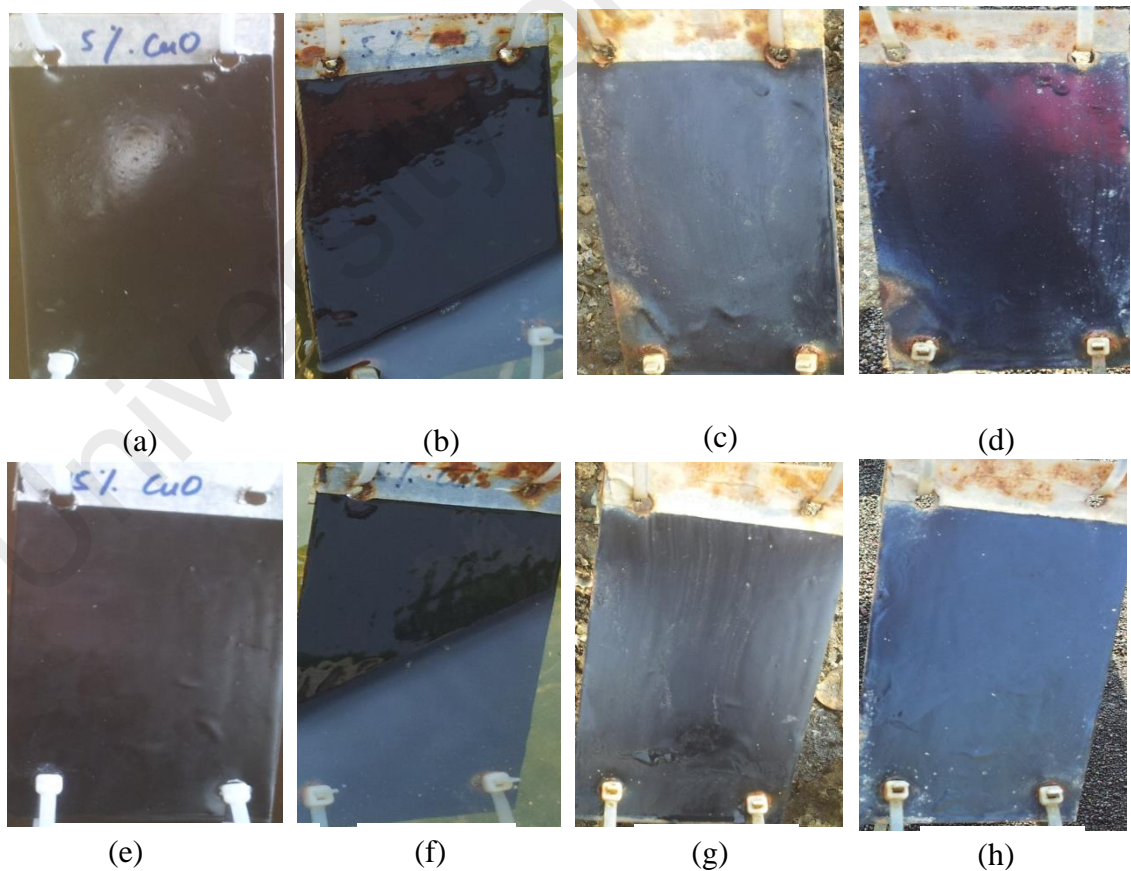


Figure 6.2: Exposure of polyester-epoxy (95%:10%) binder coating in seawater for 30 days: (a) day 0, (b) day 10, (c) day 20, (d) day 30 in Penang Island.

As can be seen from Figure 6.1 and Figure 6.2, the coated samples started showing small corrosion effects at the edge of the plates at both locations. This may be due to the seawater penetration at the coating/substrate interface. Observations of coated surface immersed at the two locations show about the same effects after 30 days of immersion.

6.2 Physical Effects for Copper Oxide Based Coating System

Samples coated with copper oxide based coating system were immersed in seawater to see the physical changes of copper oxide addition as biocides on the coated surface. The photographs taken for different percentage of copper oxide ranging from 5 % to 25% pigment volume concentration, PVC are shown in Figure 6.5 and Figure 6.6 in Lumut, Perak and Penang Island respectively.



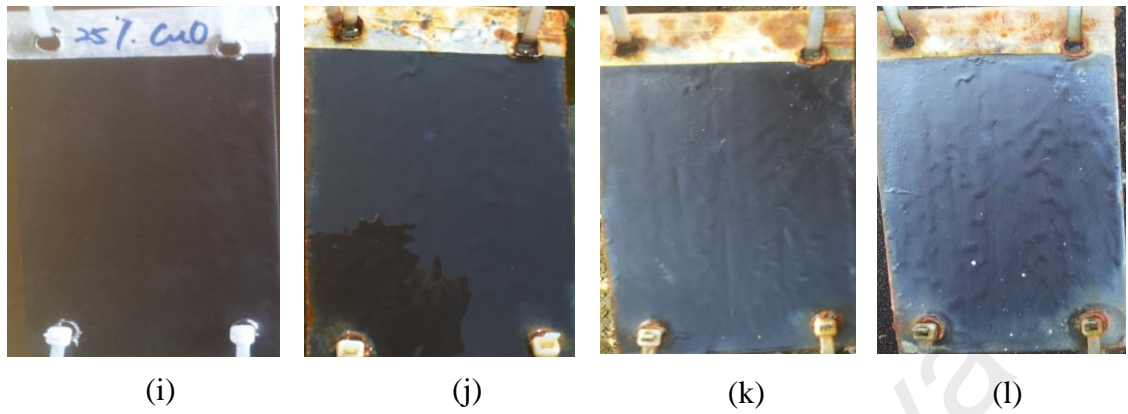
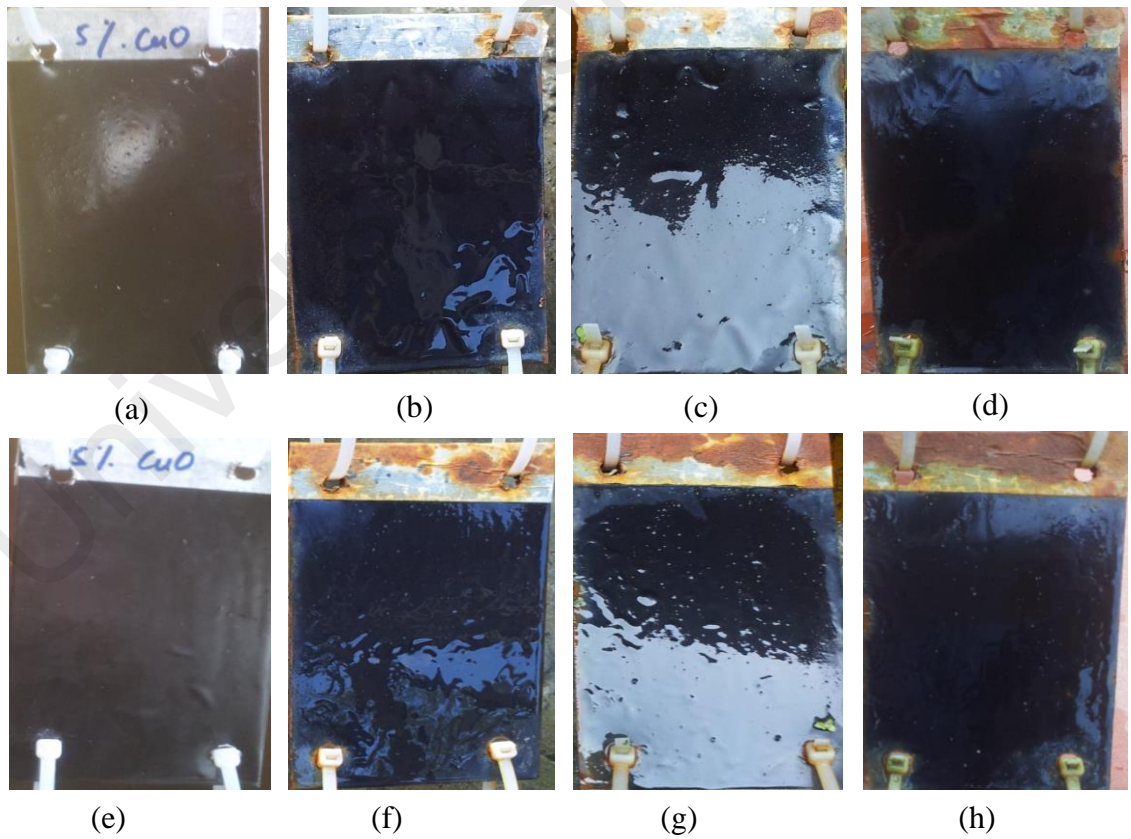


Figure 6.3: Exposure of copper oxide based coating in seawater for 30 days: 5% copper oxide - (a) day 0, (b) day 10, (c) day 20, (d) day 30; 15% copper oxide - (e) day 0, (f) day 10, (g) day 20, (h) day 30; 25% copper oxide - (i) day 0, (j) day 10, (k) day 20, (l) day 30 in Lumut, Perak



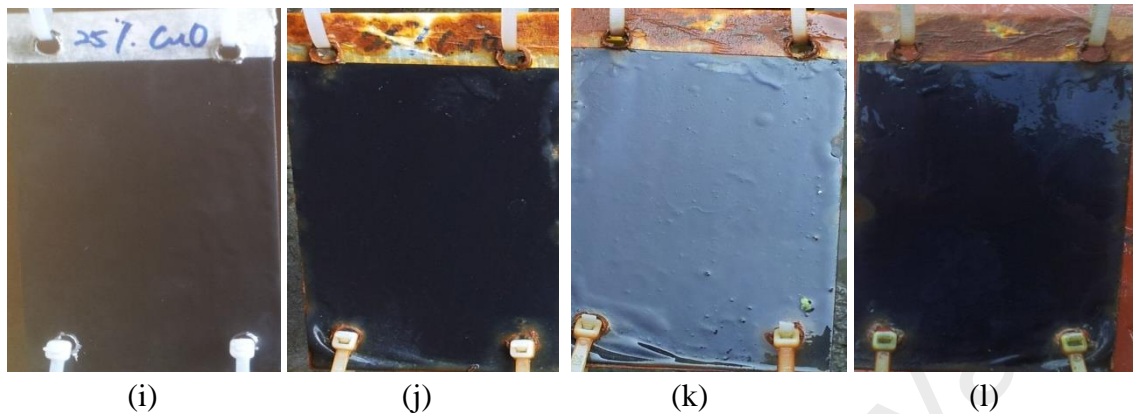
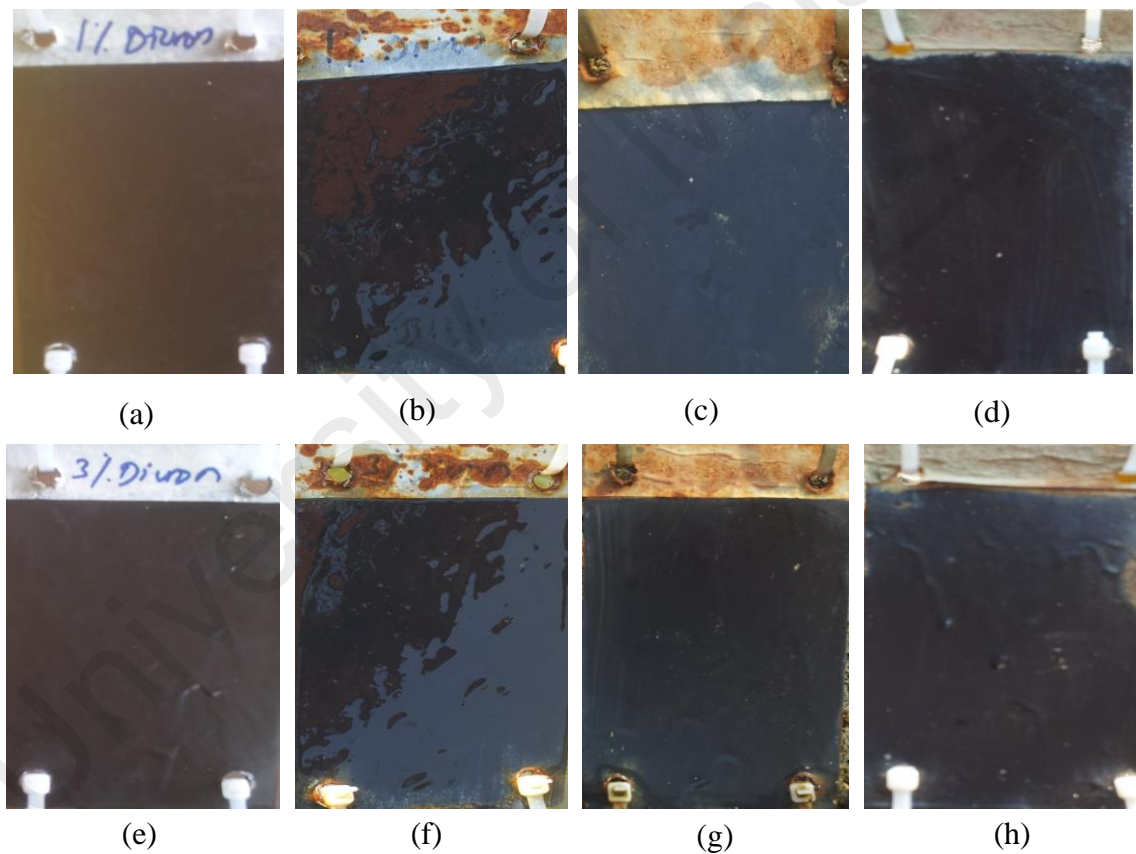


Figure 6.4: Exposure of copper oxide based coating in seawater for 30 days: 5% copper oxide- (a) day 0, (b) day 10, (c) day 20, (d) day 30; 15% copper oxide - (e) day 0, (f) day 10, (g) day 20, (h) day 30; 25% copper oxide- (i) day 0, (j) day 10, (k) day 20, (l) day 30 in Penang Island

Referring to Figure 6.3 and Figure 6.4, the addition of different percentages of copper oxide as biocide reveals that increasing pigment volume concentration, PVC makes the coated samples darker in colour. Up to the 30th day of immersion, the colour is not obviously faded. The adhesion of the coatings to the substrate was better as compared to the binder coating system. In this system, there is minimal amount of slimy layers (green algae) that were attached to the coated surface in both locations. This might be due to different salinity of the seawater in the two locations. The location of seawater exposure also might play a role to the attachment of algae on the coated surface. According to Woods Hole Oceanographic Institution (WHOI) in 1952, slime, algae and bryozoa are commonly found in lower salinity water.

6.3 Physical Effects for Copper Oxide-Diuron Based Coating System

Figure 6.5 and Figure 6.6 show the photographs taken for different percentages of diuron in copper oxide coating system ranging from 1 wt.% to 5 wt.%. The copper oxide-diuron coated system was immersed in seawater to evaluate the physical changes and analyse the antifouling characteristics of addition diuron as booster biocides. Figure 6.5 and Figure 6.6 show the photographs of copper oxide-diuron based coated samples after continuous immersion in seawater in Lumut and Penang Island.



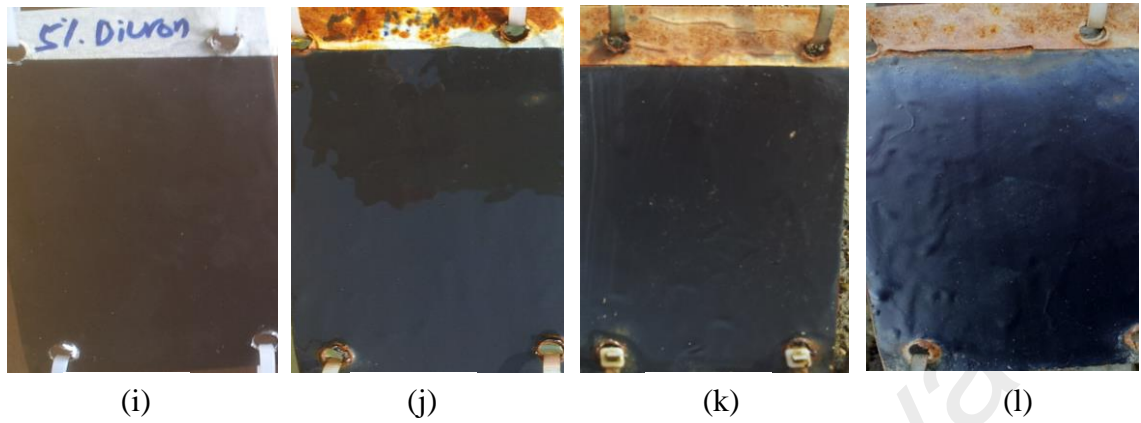
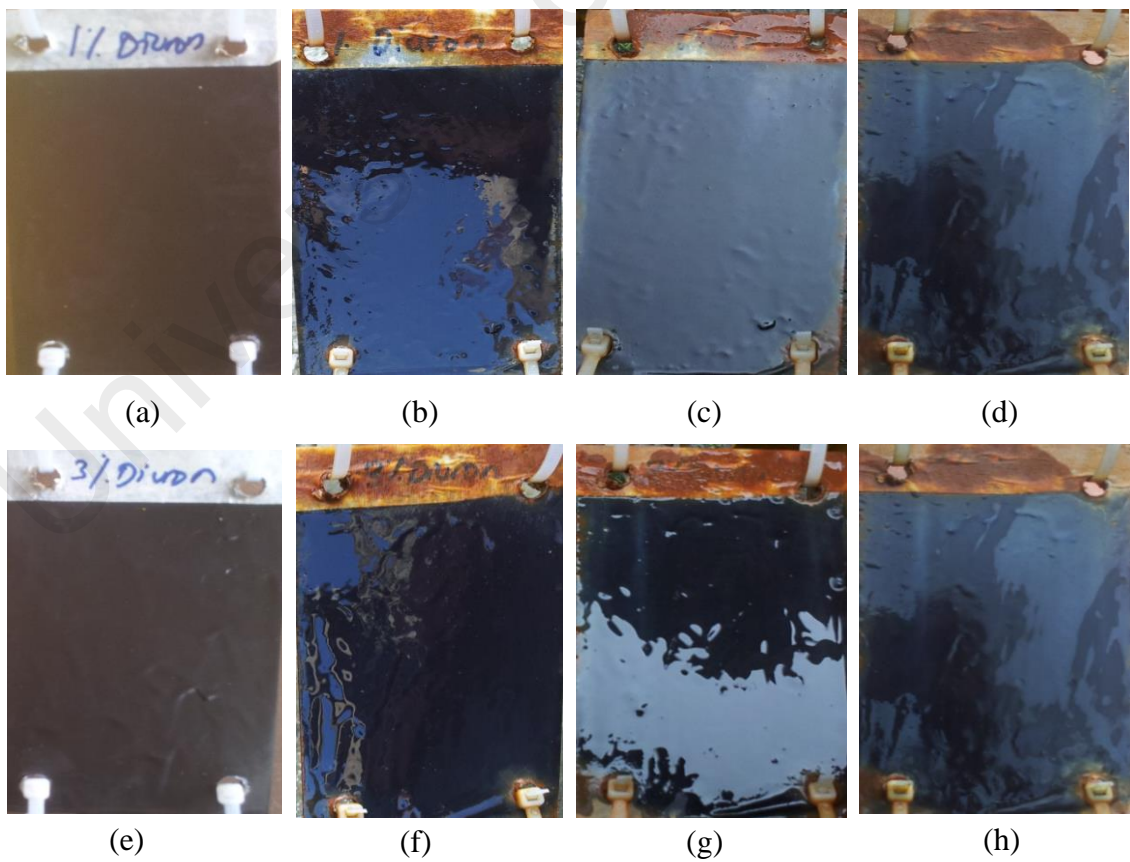


Figure 6.5: Exposure of copper oxide-diuron based coating in seawater for 30 days: 1% diuron - (a) day 0, (b) day 10, (c) day 20, (d) day 30; 3% diuron - (e) day 0, (f) day 10, (g) day 20, (h) day 30; 5% diuron - (i) day 0, (j) day 10, (k) day 20, (l) day 30 in Lumut, Perak.



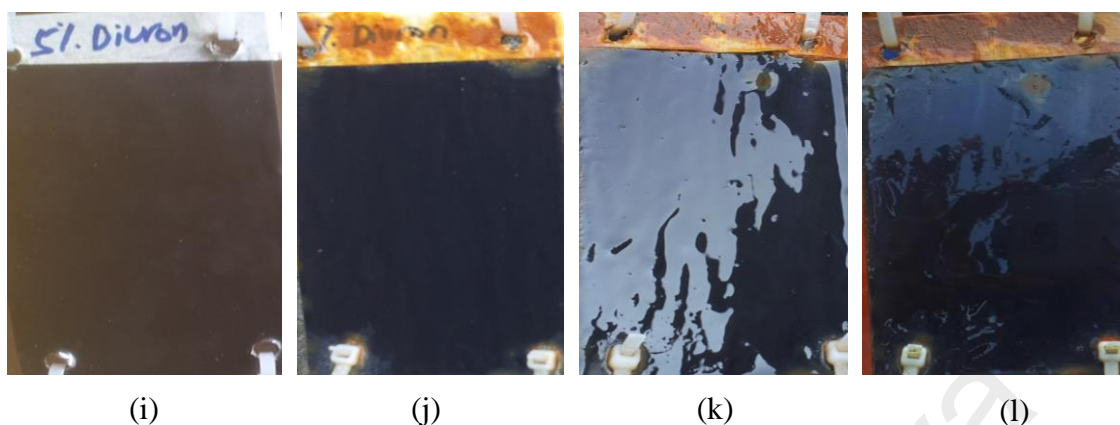


Figure 6.6: Exposure of copper oxide-diuron based coating in seawater for 30 days: 1% diuron - (a) day 0, (b) day 10, (c) day 20, (d) day 30; 3% diuron - (e) day 0, (f) day 10, (g) day 20, (h) day 30; 5% diuron - (i) day 0, (j) day 10, (k) day 20, (l) day 30 in Penang Island

Results from Figure 6.5 and Figure 6.6 showed that the addition of diuron has enhanced the physical appearance of the coatings. There are almost no biofouling adhesions on the coated surface for both locations. Comparing both the coating systems that been exposed in seawater, the copper oxide-diuron system shows the best performance of the surface and physical properties. By physical observation, the glossiness of the coated panels is also enhanced. For that, the glossiness test has been analysed and results reported in the next chapter (Chapter 7).

CHAPTER 7: RESULTS ON GLOSSINESS TEST

7.0 Introduction

Smooth and glossy surfaces are the key features and benefits to control the fouling. It is related to the amount of light reflected by the coating film on the substrate. The increasing loading amount of pigments is known to reduce the glossiness of the coatings (Dullaert *et al.*, 2011). With that reason, booster biocide diuron was added into the copper oxide antifouling coating to increase the glossiness and smoothness of the coating film. From the seawater exposure results, further investigation on glossiness was conducted.

The glossiness test was performed for different PVC of pigment and diuron addition coated samples. Gloss meter model KSJ MG268-F2 was used to determine the glossiness in each coating system. In this investigation, the reading angle of light beam used for binder coating system is at 20° while for other biocidal coated samples, an angle of 85° was selected. The selection of reading angle is based on the gloss range as shown in Table 3.5. The binder coating was used as a control to determine the effect of glossiness. Comparisons were made with the copper oxide and diuron added coating systems. The readings were obtained for the samples immersed before and after exposure in seawater in the two locations mentioned in the previous chapter (Chapter 6).

7.1 Glossiness test on Binder Coating System

The glossiness test was first done for the highest coating resistant binder coated panel, 90% polyester-10% epoxy (90P:10E) as the control sample. Gloss unit readings were taken and the average value was calculated before the graphs were plotted. Figure

7.1 below shows the gloss unit readings and the changes on surface glossiness of coatings for day 0 and day 30 after immersion in seawater.

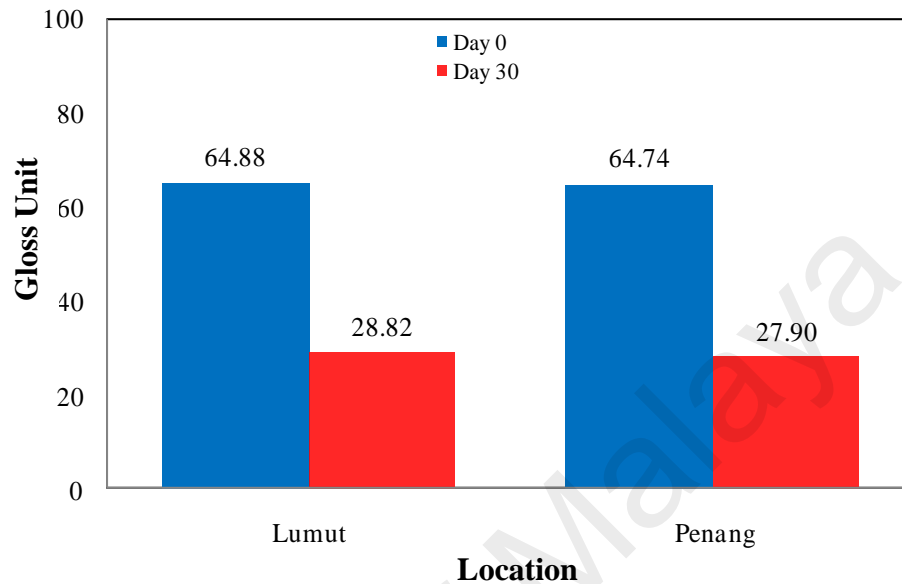


Figure 7.1: Gloss unit for binder coating system at 20°angle

Referring to the results in Figure 7.1, the gloss unit shows a decreasing value as the coated panels were immersed at the end of exposure (day 30) for both locations. It can be attributed to the increasing leaching rate as the samples were continuously immersed in seawater. However, it can be observed that gloss for both locations were about the same at the early and at the end of exposure.

7.2 Glossiness test on Copper Oxide Based Coating System

Figure 7.2, Figure 7.3 and Figure 7.4 below show the gloss unit of copper oxide based coating system. A 85° light beam angle was chosen to detect the amount of reflection intensity in gloss units.

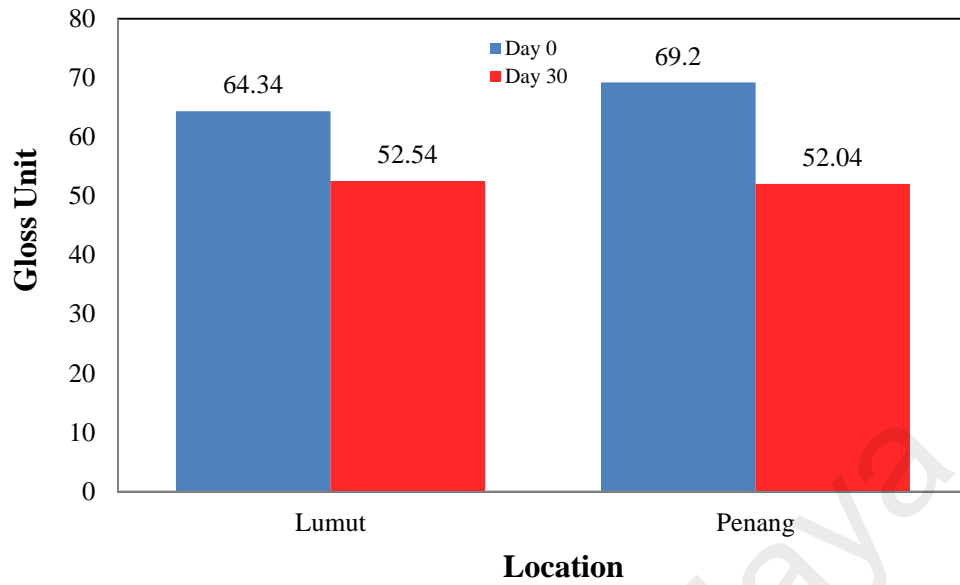


Figure 7.2: Gloss unit for 5% PVC of copper oxide based coating system at 85° angle.

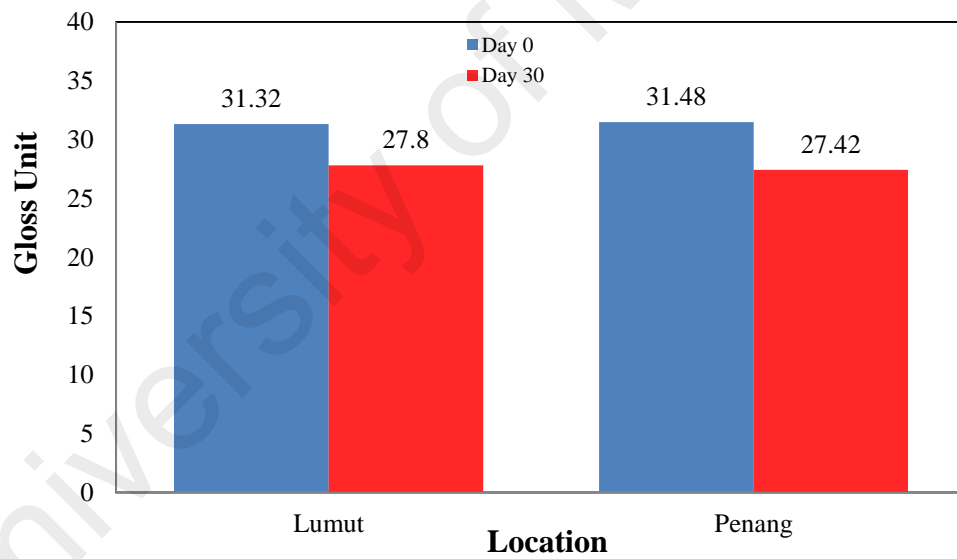


Figure 7.3: Gloss unit for 15% PVC of copper oxide based coating system at 85° angle.

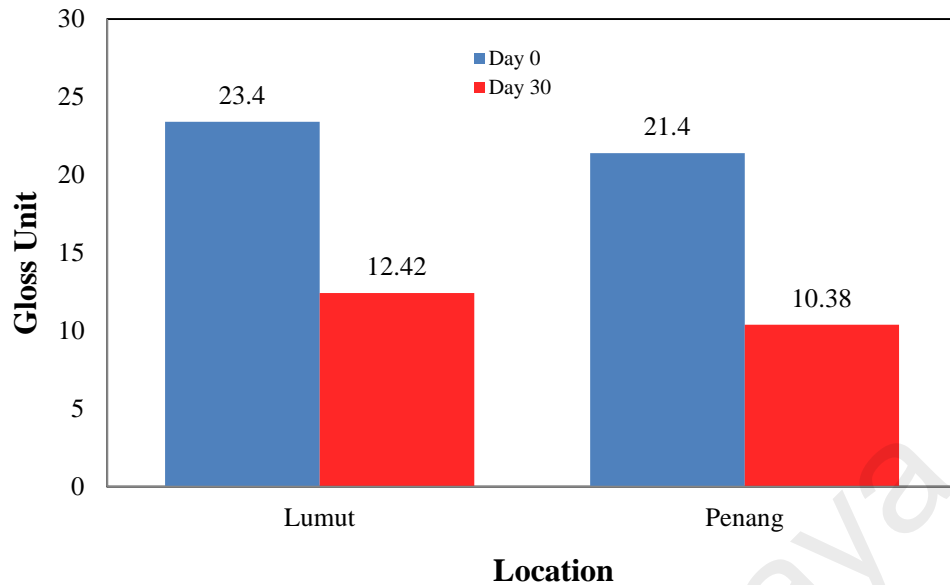


Figure 7.4: Gloss unit for 25% PVC of copper oxide based coating system at 85° angle.

From the results, it can be observed that the value of gloss unit were decreased with increasing amount of copper oxide added ranging from 5 PVC % to 25 PVC %. The highest copper oxide concentration added in the coating system gives the lowest value of gloss unit. This may be due to the dispersion of pigment particles in the binder coating system that has increased the roughness of the coating surface as the concentration of biocide increased (Dullaert *et al.*, 2011). At the end of exposure in seawater, the value of gloss unit decreases that can be attributed to the chalking effect after the leakage of the copper oxide particles into the seawater. Similar observation has been reported by Kiosidou *et al.*, in 2014, where the chalking effect has reduced the glossiness of the coated surface for the developed epoxy based antifouling coating.

7.3 Glossiness test on Copper Oxide-Diuron Based Coating System

Figure 7.5, Figure 7.6 and Figure 7.7 below show the glossiness test results for the copper oxide-diuron based coating system. The same range of percentage of diuron (1 wt. % - 5 wt. %) was added to the copper oxide based coating system and the glossiness test was then carried out.

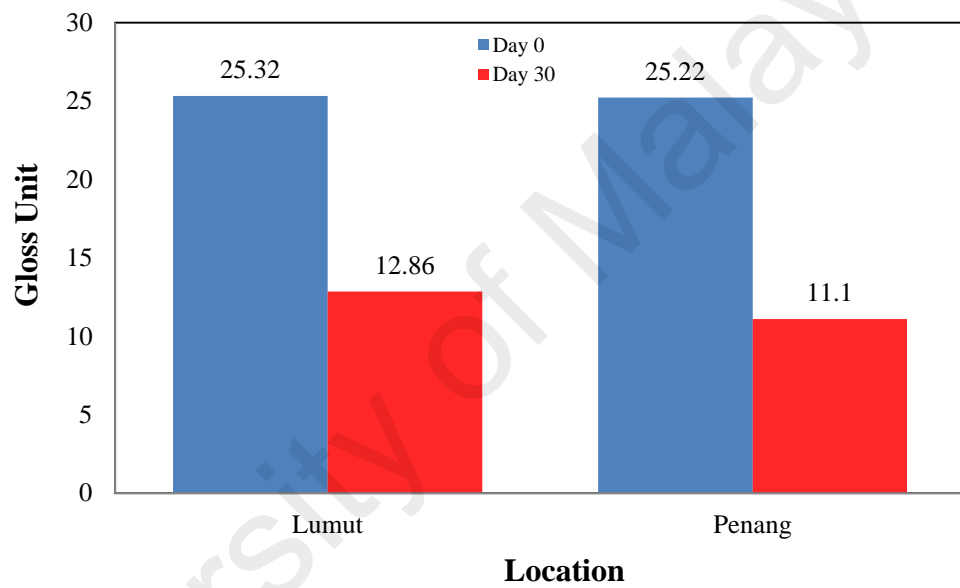


Figure 7.5: Gloss unit for copper oxide-1 wt.% diuron based coating system at 85° angle.

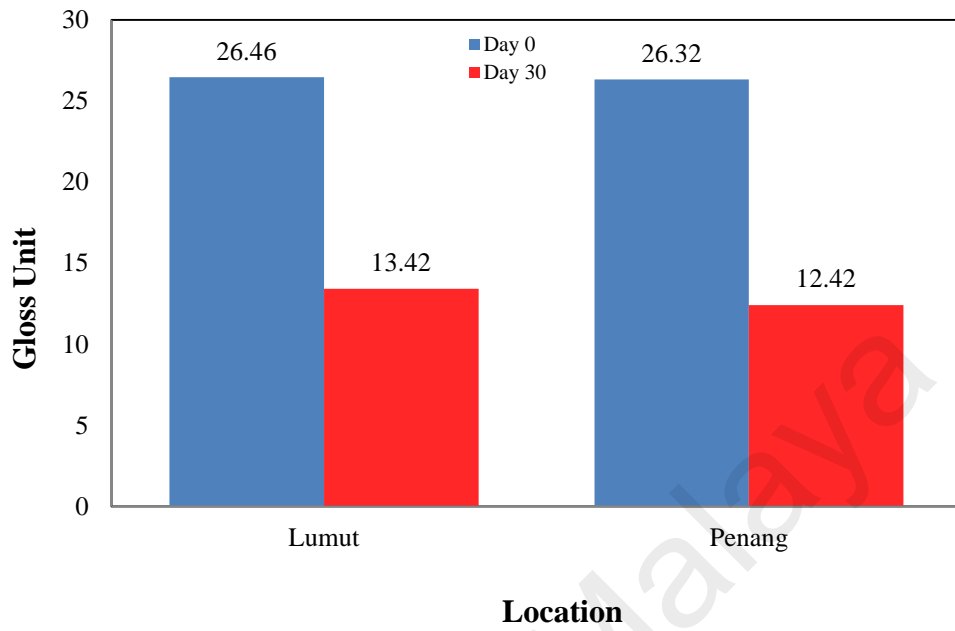


Figure 7.6: Gloss unit for copper oxide-3 wt.% diuron based coating system at 85° angle.

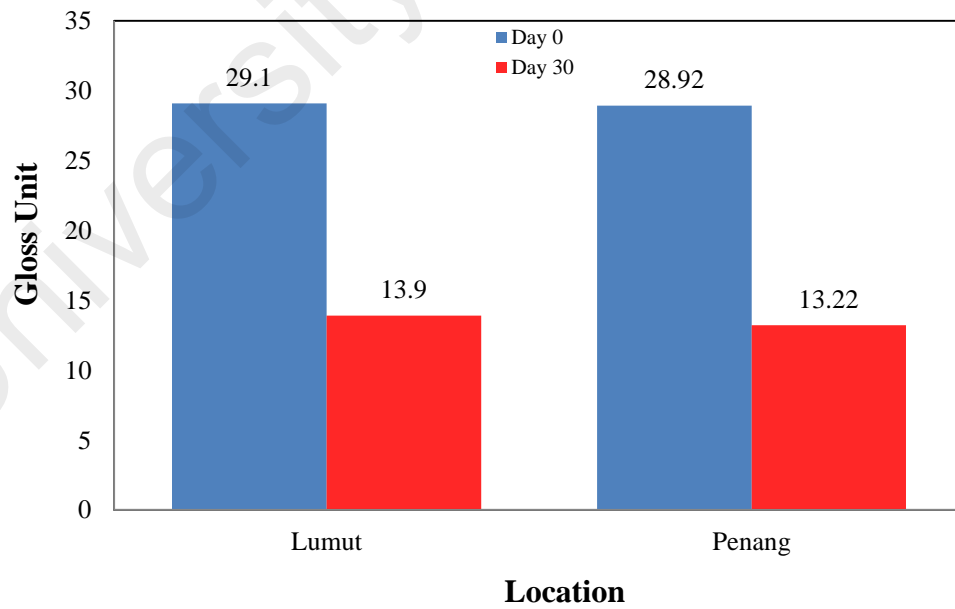


Figure 7.7: Gloss unit for copper oxide-5 wt.% diuron based coating system at 85° angle.

Referring to the above results, the gloss unit increased with increasing amount of diuron added in the coating system. The highest gloss unit was observed at 5 wt. % of diuron concentration in the coating system which is at 29.1 and 28.92 gloss unit for Lumut and Penang Island respectively. The glossiness was observed to decrease at the end of exposure in seawater for all samples. The increasing gloss unit with higher concentration of diuron in the coating system may be due to the increase of homogeneity between copper oxide particles and the resins. Poor pigment dispersion may lead to the increase of the surface roughness (Duivenvoorde *et al.*, 2002). In this work, the addition of diuron helps to increase the glossiness of the coating film surface by increasing the degree of pigmentation within the resin binder.

CHAPTER 8: RESULTS ON SURFACE MORPHOLOGY STUDIES

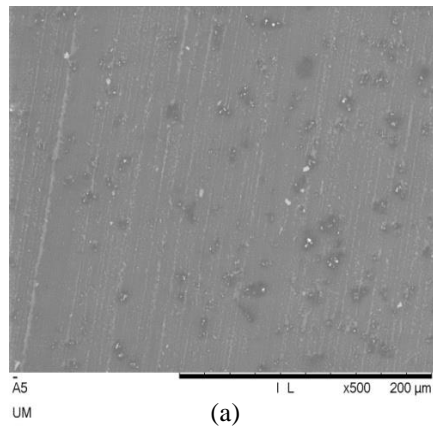
8.0 Introduction

Previous studies have demonstrated the effect of adding biocides and booster biocides to understand the antifouling coating characteristics. The morphology study is one of the popular techniques to investigate the surface characteristics of a coating film. The effect of pigments or biocides addition in a coating system can be determined using scanning electron microscope (SEM).

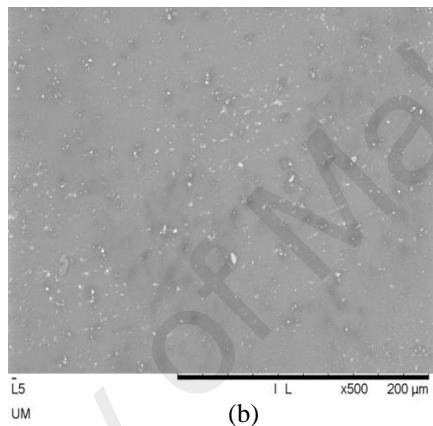
In this work, scanning electron microscopy (SEM) was carried out for copper oxide and copper oxide-diuron antifouling coating systems which were applied on a glass slide to see the microscopic changes to the coating surface before and after immersion in seawater. The TM3030 tabletop microscope from Hitachi High-Technologies (Germany) was used to study the surface morphology of the exposed area for the samples collected from the field test with the same magnification of 500 x and 5kV of accelerating voltage.

8.1 Surface Morphology of Copper Oxide Based Coating System

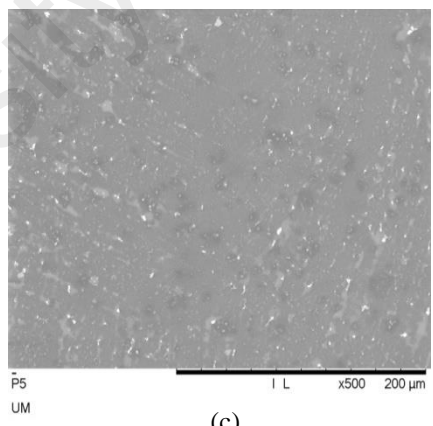
Figure 8.1, Figure 8.2 and Figure 8.3 show the SEM micrographs obtained from SEM study for 5% PVC, 15% PVC and 25% PVC for both seawater exposure locations. The effect of adding different pigment volume concentration and the real exposure effect for copper oxide biocides coating system can be investigated from this study.



(a)

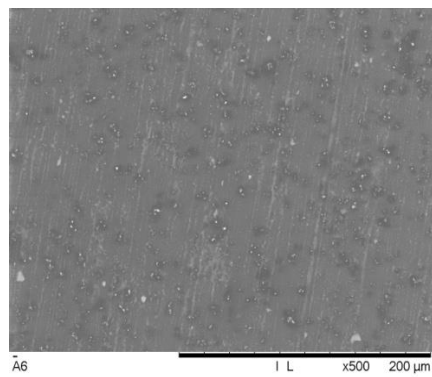


(b)

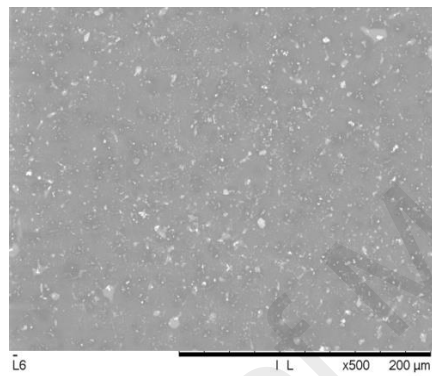


(c)

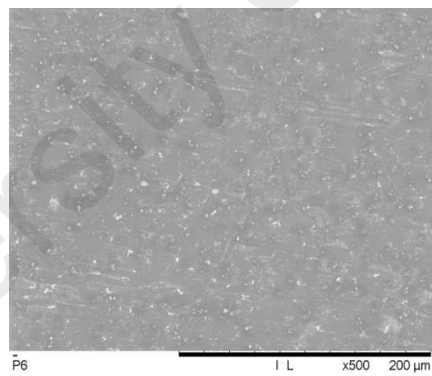
Figure 8.1: Surface morphology images for copper oxide coating system for 5% PVC; (a) before immersion in seawater, (b) after immersion at Lumut, Perak, (c) after immersion at Penang



(a)

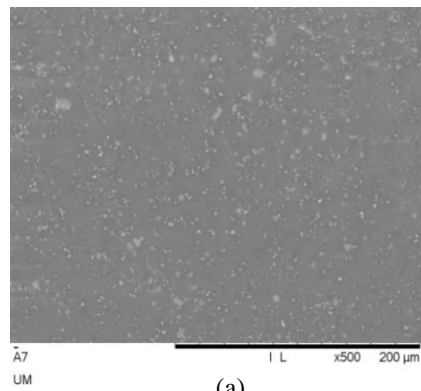


(b)

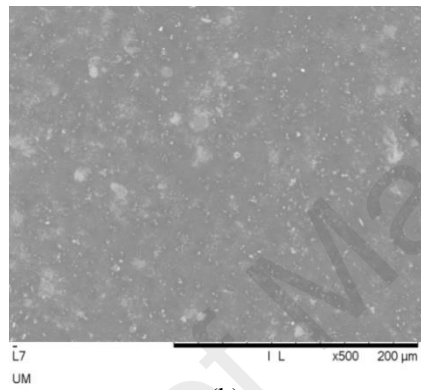


(c)

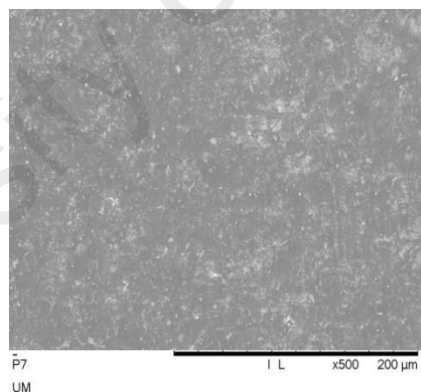
Figure 8.2: Surface morphology images for copper oxide coating system for 15% PVC; (a) before immersion in seawater, (b) after immersion at Lumut, Perak, (c) after immersion at Penang



(a)



(b)



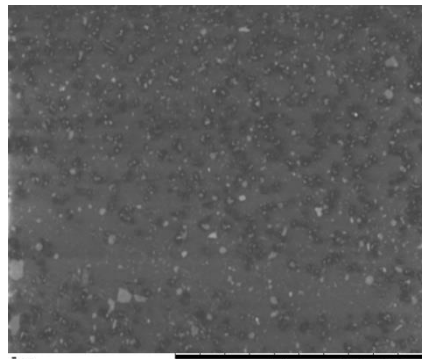
(c)

Figure 8.3: Surface morphology images for copper oxide coating system for 25% PVC; (a) before immersion in seawater, (b) after immersion at Lumut, Perak, (c) after immersion at Penang

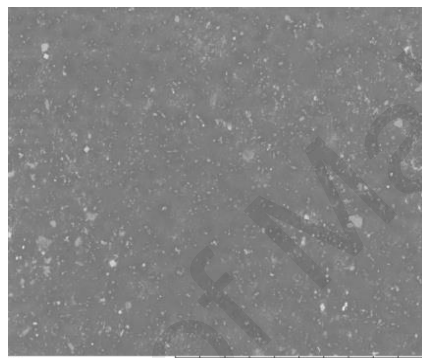
From the SEM results in Figure 8.1, Figure 8.2 and Figure 8.3, it can be seen that increasing the pigment volume concentration will result in an even distribution of the pigments in the coating system. The chalking effect on the copper oxide based coating system was observed after the coated surface has been immersed in seawater for 30 days. This may be due to the biocides leaching from the coating film into the seawater. Similar images were obtained by Oikonomou *et al.*, (2012) where Cu^{2+} based polymeric biocidal material antifouling coatings were developed.

8.2 Surface Morphology of Copper Oxide - Diuron Based Coating System

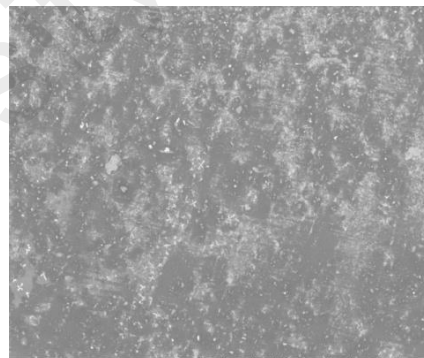
Figure 8.4, Figure 8.5 and Figure 8.6 show the SEM micrographs for diuron addition into the copper oxide based coating system ranging from 1 wt. % to 5 wt. %. The addition of diuron as booster biocide is known to improve the coating characteristics as presented in the previous chapters. Hence, it is expected that the surface of the coating for the copper oxide-diuron system to be less affected by seawater.



(a)

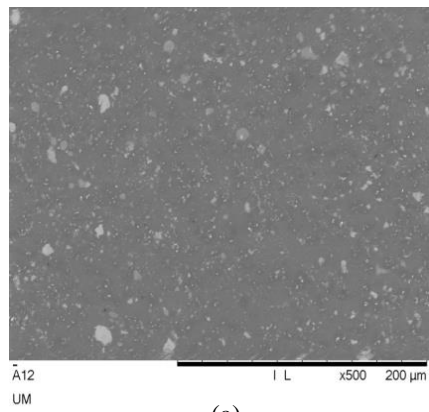


(b)

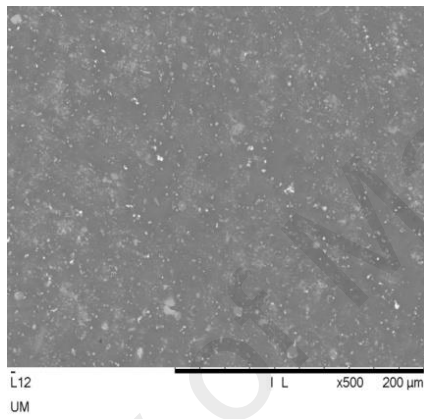


(c)

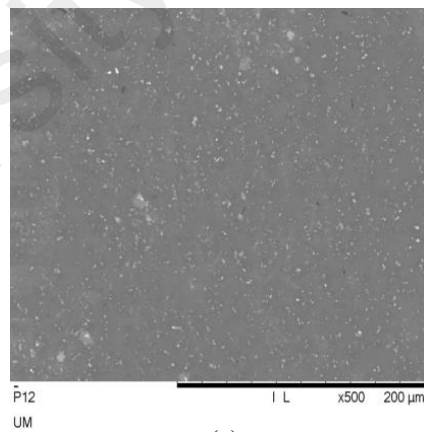
Figure 8.4: Surface morphology images for copper oxide-diuron coating system for 1 wt % diuron; (a) before immersion in seawater, (b) after immersion at Lumut, Perak, (c) after immersion at Penang.



(a)

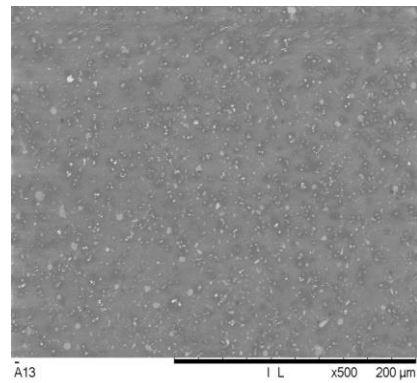


(b)

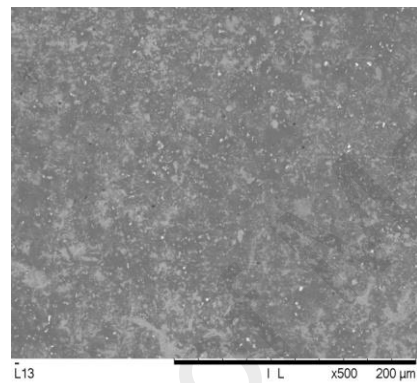


(c)

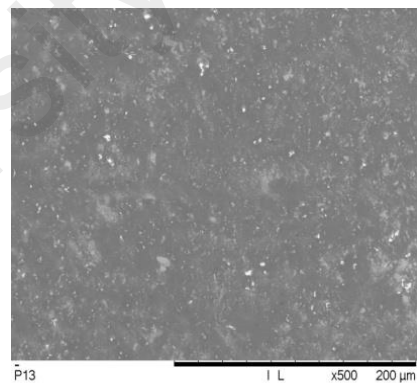
Figure 8.5: Surface morphology images for copper oxide-diuron coating system for 3 wt % diuron; (a) before immersion in seawater, (b) after immersion at Lumut, Perak, (c) after immersion at Penang.



(a)



(b)



(c)

Figure 8.6: Surface morphology images for copper oxide-diuron coating system for 5 wt % diuron; (a) before immersion in seawater, (b) after immersion at Lumut, Perak, (c) after immersion at Penang.

From the results obtained in Figure 8.4, Figure 8.5 and Figure 8.6, the diuron addition in both biocide systems shows an improvement of the surface morphology where smoother surface was obtained as compared to the previous systems. The increasing composition of diuron in the copper oxide-diuron coating system also shows a homogeneous particle distribution in the resin. Reduced chalking effects can be seen with addition of diuron in the coating system. Besides, the surface morphology of copper oxide-diuron coating system showed no adhesions of macro and microorganism towards the end of exposure in seawater. This surface morphology studies are in agreement with physical test results reported in Chapter 6.

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CHAPTER 9: DISCUSSION

It is the objective of this thesis to study the antifouling properties on the polyester-epoxy based coatings. It is very important to determine a good thermal and mechanical binder coating to evaluate the performance of a coating system. Proper measurement and analysis techniques need to for a proper evaluation of these properties to ensure the coating performance. It is also the intention of this thesis to study the effect of adding copper and copper oxide as biocides; and diuron as booster biocides to enhance the coating resistance or also known as corrosion resistance and other surface properties of the coated panels. As a means to understand the effect of biocides composition on the coating resistance, elementary studies in different types of electrolytes were carried out to obtain the leaching concentration of the biocides on the coated panels. The real exposure in seawater was done in two locations to study the corrosion effect of the coatings on the mild steel substrate. The surface morphology effect study was then carried out for the immersed samples which were collected after 30 days. The physical effect study was finished by determining the gloss effect for the samples exposed in seawater to explain the effect of adding biocides/booster biocide on the coated surface. Hence, this may explain the antifouling characteristic of the prepared coating system.

To study the performance of polyester-epoxy binder coating, the characterization of polyester and epoxy binder systems were discussed in Appendix A. The study of mechanical properties and thermal characteristics and adhesion power between polymer-substrate of the polyester/epoxy binder resin were carried out using DSC, FTIR and pull off adhesion test. The results in Appendix A shows that the glass transition temperature, T_g decreases with increasing amount of epoxy. This shows that the polymeric structure of the binder coating has increased the flexibility of polymer binder

coating system and improved the thermal property of the binder coating. Similar results were reported by Cao *et al.*, (2008) that the decreasing value of glass transition temperature, T_g after adding the amount of polyester to the epoxy resins. This has resulted the minimum value of internal stress of the coating that hence demonstrated better performance of mechanical strength and also the thermal stability of the modified epoxy powder coatings.

From the FTIR analysis, the cross-linking between the resins can be explained since there were shifting in peaks of the functional groups. The cross-linking between polyester and epoxy resins can be confirmed due to the existence of the stretching asymmetrical C-C band and contraction of the C-O band (Deen *et al.*, Castela *et al.*, 2000). The peaks observed at 1685 cm^{-1} and 1725 cm^{-1} indicates the presence of ketone functional group C=O, which related to the adhesion between the coating and substrate (Huybrechts and Tanghe, 2007). With increasing concentration of epoxy, the C=O peak was observed to decrease in intensity. This explains the poor adhesion of the coating to the substrates. The presence of the OH functional group at the range of 3370 cm^{-1} has been reported by Li *et al.*, (2007) to play role that helps the adhesion and cross-linking process within samples, that can also been observed in all samples as shown in Figure A.3. It is to be noted that the results in Appendix A was accepted to be published in Pigment and Resin Journal in July 2015.

Increasing amount of epoxy will show more brittleness behavior of the binder coatings. This result shows an agreement with the DSC results which give the smallest value of glass transition temperature that can explain better adhesion power of the coating to the substrate.

Variation of coating resistance with 30 days of exposure in 3.5% of sodium chloride as artificial seawater has been depicted in Chapter 4. It is noted that the polyester and

epoxy based coating system has been studied by several workers e.g. Naderi *et al.*, (2004) who reported on two corrosion test method using electrical impedance spectroscopy (EIS) and open circuit potential in function of time; Cao *et al.*, (2001) who studied the internal stress of modified epoxy resins with polyester and related with the thermal studies and morphology; Chakradharet *et al.*, (2011) who reported on mechanical, thermal and morphological properties of epoxy/polyester blend nanocomposites; Prabu and Alagar (2004) who studied on the mechanical and thermal of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings; Barletta and Bellisario (2011) who characterized the mechanical behavior of free-standing epoxy-polyester films using differential scanning calorimetry (DSC) and dynamic-mechanical analysis (DMA) and Jahani (2011) who reported on the effect of epoxy-polyester hybrid resin on mechanical properties, rheological behavior, and water absorption of polypropylene wood flour composites.

The value of coating resistance in all coating systems decreased with the time of exposure in artificial seawater (3.5% NaCl). The decreasing value of coating resistance by time of immersion in artificial seawater was reported by many researchers (Liu *et al.*, (2013), Grundmeier *et al.*, (2000), Sathiyarayanan *et al.*, (2008), Kamaraj *et al.*, (2011), Santana *et al.*, (2012), Patil *et al.*, (2012)) who reported that it is related to the increase of the water absorption to the coatings (Patil *et al.*, (2012), Mirabedini *et al.*, (2003), Ramesh and Vasudevan (2012), and Monero *et al.*, (2012). In the polyester-epoxy binder system, the highest value of coating resistance obtained at 2.894×10^8 ohm at the end of exposure in 3.5% NaCl for sample containing 90% of polyester. The effect of blending has been reported to increase the performance of the binder coating such as the thermal stability, mechanical properties, adhesion properties and also the corrosion resistance of the coated surface (Cao *et al.*, 2001; Anand Prabu and Alagar, 2004; Mafi *et al.*, 2008; Patil *et al.*, 2012; Ramesh *et al.*, 2011; Ramesh *et al.*, 2013). Epoxy resin

has been reported to have good mechanical, toughness and corrosion resistance properties although has brittleness behaviour and poor resistance to the impact and crack propagation (Liu *et al.*, 2005). Polyester resin has high tensile and flexural strength and high resistance to softening and deformation at high temperature (Ananda Kumar *et al.*, 2006). By combining the two resins, the coating resistance performance of the polyester-epoxy binder has been increased and the binder can be used for further application of corrosion resistance and antifouling prevention.

In addition of copper and copper oxide in the biocides coating system, the value of coating resistance is increased at the end of exposure as compared to the polyester-epoxy binder coating system. The higher value of coating resistance at day 30 obtained for both copper and copper oxide based biocide coating system are achieved at 25 PVC percentage of biocide. The values obtained are 5.701×10^8 ohm and 7.107×10^8 ohm for copper and copper oxide based coating respectively. Similar results reported by Ramesh and Vasudevan (2012) and Ramesh *et al.*, (2011) whom also have obtained the value of coating resistance at the same order of magnitude after 30 days of exposure in artificial seawater. According to Amirudin and Thierry (1995), a coating system has good anticorrosion properties if the coating resistance is exhibited more than $\sim 10^7$ ohm. From the results shown in the biocide coating system, both copper and copper oxide based coatings obtained the value of coating resistance ranging from $\sim 10^9$ ohm to $\sim 10^7$ ohm from the beginning until the end of immersion with 3.5% NaCl. Reports from Bacon *et al.*, (1948) and Greenfield and Scantlebury (2000) also have illustrated the schematic value for good, fair and poor of coating resistances in the plot of coating resistance versus time of immersion in artificial seawater.

The highest pigment volume concentration (PVC) for each copper and copper oxide biocide system shows that the addition of more concentration of pigments has led to the

increase in R_c . 25 % of PVC for copper and copper oxide were chosen to study the metal/metal oxide leaching. From the results obtained from Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), copper oxide based coating showed the highest value of leaching concentration in real seawater. The least value of leaching concentration was observed for the distilled water. The result may be due to the reaction between the chloride ions in the seawater with the biocides in the coatings. According to Fick's Second Law, the rate of water diffusion will increase with time of immersion (Bonora *et al.*, 1996; Mirabedini *et al.*, 2003; Prosek and Thierry, 2004; Lazarevic *et al.*, 2005; Ramesh and Vasudevan, 2012). As the time is increased, the biocides leaching concentration also increased for both systems. The water absorption into the copper and copper oxide coatings on the mild steel substrate is observed to increase from day 1 to day 30 in the electrolytes. The higher value of leaching concentration in copper oxide based coating system showed that the degree of dispersion of pigments is higher than the copper based coating system. From the results obtained in Chapter 6, the leaching rate of the copper oxide based coating system obtained is higher at the end of exposure in seawater. Report by Cima and Balarin in 2008 obtained the leaching rates from 40 to 60 mg/cm² per day for the developed self-polishing paints and hard-matrix paint for initial exposure in Venice Lagoon. Referring to the report by Asbeck and Loo (1949), the appearance and behavior of a coating also can be described with the degree of dispersion for the critical pigment volume concentration, CPVC. The effect of real exposure in seawater of coated panels in different pigment volume concentrations are discussed in Chapter 6.

The real exposure in seawater was carried out for the coated panels in two locations in Malacca Straits. Lumut, Perak and Penang Island were chosen as the preference to analyse the effect of seawater environment to the coated panels. The results shown in Chapter 6 were started with the physical effect for the polyester-epoxy binder coated

panels. For both locations, it seems that the corrosion effect has started to be observed after 20 to 30 days of exposure in seawater at the edge of the coated surface. This may be due to the penetration of electrolyte that has been started at the lower thickness of coatings that might be the results for the delamination of coating to that area. During the coating curing processes on the mild steel panels, the thickness of the coating cannot be controlled. It maybe resulted to thinned coatings at the edge of the panels. However, the coatings show good results at the middle of the coated panels without any corrosion effect. Only small slimy layers (biofilm) observed and this can be easily removed from the surface. In the copper oxide biocide coating system, different percentage of pigment volume concentration, PVC of copper oxide coated panels has been exposed in the seawater for 30 days. In addition of 5% to 25% of PVC of copper oxide, it can be seen that better surface effect with increasing amount of PVC which is at 25 % PVC of copper oxide content. The faded colour of the pigment or chalking effect can also be seen in both locations of exposure may be due to the biocide leaching by time of immersion. Slimy layers were also observed at the Penang Island seawater exposure. This may be due to the location is near the muddy type ground that green algae are more produced in that area. The high leaching rate of copper oxide might be the reason of the antimicrobial adhesion on the coating system. The addition of booster biocides (diuron) in the copper oxide antifouling coating system is to increase the performance of antifouling effect of the coatings. Referring to the results in Figure 6.5 and Figure 6.6, the addition of diuron into the copper oxide biocides based coating system has increased the glossiness and colour effect of the coated panels. The biofilm adhesion from the green algae is also reduced on the coated surface. Besides, chalking effect also decreased as compared to the copper oxide biocides coating system. The physical effect results showed the best surface effects as the glossiness and antimicrobial adhesion are improved. There are no slimy layers or other types of microbial adhesion and the color

of the pigments are more stable as can be seen at the end of exposure. With the results in all the coating systems prepared, we can conclude that the copper oxide-diuron system shows the best performance of the surface and physical properties.

In Chapter 7, the surface properties of the coated samples were examined using glossiness test to study the surface effect of the prepared coated panels in seawater. As been reported by other researchers, the glossy surface might leads to the better appearance of a coating film and improves the surface roughness (Ozcelik *et al.*, 2012; Dullaert *et al.*, 2011; Barletta *et al.*, 2007; Jarnstrom *et al.*, 2008). In this work, the glossiness test was done using a glossmeter following the standard ISO 2813. The readings were taken for selected samples that have been exposed in the seawater. Based on the results in Figure 7.1, the binder coated samples shows a high gloss unit at 64.88 and 64.74 for seawater exposure in Lumut and Penang respectively and dropped to less than 50% of the gloss unit after 30 days have been immersed in the seawater. The surface degradation may be due to the delamination of the coating and reduced the surface roughness by time (Hinderliter *et al.*, 2006). According to the report by Huybrechts and Tanghe in 2007, the higher surface hardness and reflection of an object to the surface, the more brilliant the coating film will appear. Referring to Figure 7.2 to Figure 7.4, the gloss unit of the copper oxide coating system seems to be reduced with increasing concentration of copper from 5% to 25 % of PVC. This result was similar to the report by Vasely and co-workers in 2012 for the calcined kaolins coating system that exhibit lower value of gloss unit with higher amount of pigment volume concentration, PVC. After the exposure in seawater, the gloss unit also shows a reduced value of gloss unit for both locations. The increased percentage of pigment volume concentration, PVC in copper oxide biocides coating system shows that the surface become less glossy and this may leads to the higher surface roughness of the coating films (Dullaert *et al.*, 2011). According to Erich *et al.* (2008), the higher the percentage of PVC, more porous

structure may be obtained. This will cause the increased in water absorption from the coating through the steel substrate in which the delamination can take place. However, report by Barletta and Bellisario in 2011 shows that the roughening of the coated surface may leads to the better adhesion of the film. In their report, other surface profiles via surface topography and roughness measurement also has been reported. Schlesing and co-workers in 2003 and 2004 also reported that the surface treatment, amount and type of pigments can improve the yield strength of the coating. This shows that although the higher percentage of pigments may decrease the glossiness of the coating film, the mechanical strength and the adhesion of the coatings can be improved.

On addition of diuron into the copper oxide based coating system, the results show that the gloss unit was increased as we increase the percentage of diuron from 1 wt.% to 5 wt.%. With continuous immersion in seawater, the gloss unit was reduced in all compositions of copper oxide biocides coating system. It may be due to the increase of biocides leaching of biocidal species into the seawater. In virtual observation also we can see that the faded or chalking effect was reduced in diuron-copper oxide coating system. As compared to the copper oxide biocides coating system, the copper oxide-diuron coating system shows the best results when the surface glossiness was increased after the immersion in seawater for both locations. The increasing glossiness result with diuron addition into copper oxide biocide coating system implies that the surface effects can be enhanced by decreasing the roughness and increased the smoothness of the coated samples. To study the morphology effects before and after immersion in seawater, scanning electron microscope was used to see the surface changes for selected samples for each system.

The SEM micrographs for the copper oxide based coating system are shown in Chapter 8. Comparison can be made between the micrographs of addition of biocides

and booster biocides of the coating system after being exposed in the seawater. The addition of different pigment volume concentration of copper oxide in the polyester-epoxy binder system shows that the dispersion of the biocides particle are more evenly distributed within the polymer binder with increasing amount of PVC. Before the seawater exposure, smoother surface was obtained at lower percentage of PVC for each biocide based coating system. The degree of pigmentation at different percentage has changed the morphology of the coatings. Similar result was reported by Erich and co-workers in 2008 where the different percentage of PVC has influenced the surface morphology of the alkyd coatings which shows smoother surface at lower percentage (< 50% PVC) of the coating. At the end of exposure in seawater, the surface effect for copper oxide biocide based coated panels can be seen in the SEM micrographs for both locations. In the copper oxide based coating system, the SEM micrographs show that the particles distribution in the samples are more even with increasing amount of PVC. At the end of exposure, the SEM micrographs show that the addition of copper oxide gives similar surface effect in Lumut, Perak as compared to the micrographs shown for the seawater exposure in Penang. The environment and the different salinity can be the reason of the different results obtained in both locations. The small adhesion of slimy layers and chalking effect also can be observed in copper oxide biocides coating system the end of exposure in both locations. The samples also show a minimal chalking effect and slimly layers for the coating system. In the booster biocides system, the effect of diuron addition has also been observed. The SEM micrographs results show better surface effect of the copper oxide-diuron based coating system as compared the copper oxide based coating system. Results from surface morphology study show smoother and lesser chalking effect on the booster biocide based coatings films. The microbial adhesion and chalking effect also can be reduced with the addition of diuron in the coating system. It has also good adhesion between copper oxide-diuron coating and the

mild steel substrate and the coating system shows the best microbial prevention. The surface morphology gives the stable effects in the copper oxide diuron coating system that improves the characteristics of the antifouling coating.

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CHAPTER 10: CONCLUSIONS & SUGGESTIONS FOR FURTHER WORK

In this thesis, four types of copper and copper oxide based coating system have been prepared and applied on the mild steel panels using the brushing technique. The coating systems have been characterized using electrical impedance spectroscopy (EIS), Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES), real exposure in seawater, scanning electron micrographs (SEM) and gloss meter to study the effect of antifouling of the coatings.

The DSC result shows that in addition of more composition of polyester to the polyester/epoxy binder resin has decreased the glass transition temperature. The increase of the flexibility of the polymer chain in the binder coatings system had led to increase of adhesion power which also promotes better mechanical properties and thermal stability of the coating system. FTIR analysis can determine the functional group and cross-linking occur in the coating samples.

The electrical impedance spectroscopy (EIS) measurement has been carried out to determine the coating resistance, R_c of all coating samples. Data from the impedance measurements have been analyzed to obtain the Bode plots which used to calculate the values of coating resistance for each coating system. For both biocides coating systems, the decreasing value of coating resistance, R_c with time of immersion can predict the water absorption mechanism of the coated samples. At the end of exposure, the best values of coating resistance for copper and copper oxide biocide coating system were 5.7×10^8 ohm and 7.1×10^8 ohm respectively.

The sufficient leaching concentration of the biocides released in the electrolyte from a coating film will lead to the better antifouling properties. The leached biocides may kill and prevent the adhesion of the microbes and fungi on the surface of the coated panels. The higher difference of biocides concentration leached, the higher the rate of leaching. From the results obtained in Figure 5.1 and Figure 5.2, the leaching concentration of both copper and copper oxide is increased with the immersion time. In both biocide systems, the highest concentration and the least concentration were found in seawater and the distilled water respectively. The higher amount of dissolved ions in seawater is one of the reasons that led to the higher leaching rate of copper oxide based biocide coating system as compared to the artificial seawater and distilled water. In seawater, the highest biocide leaching concentration is at 140.80 mg/L for copper based biocide system and 176.26 mg/L for copper oxide biocide system. At the end of exposure in seawater, the leaching rate of copper oxide biocide also showed higher value of 18.65 mg/cm² per day as compared to copper biocide leaching rate at 14.90 mg/cm² per day.

The real seawater exposure tests for copper oxide and copper oxide-diuron based antifouling coatings were conducted in Lumut in the state of Perak and along the coast at Pulau Betong in Penang Island. In copper oxide biocide antifouling coating, the addition of copper oxide has prevented the adhesion of microorganism and barnacles on the coated surface. By the leaching of the copper oxide into the seawater, it has killed the microorganism such as green algae and fungi before they can adhere on the coating surface. From the photographs taken, it is shown that the effect of seawater environment in both locations showed not much different in physical effect on the coated samples. The addition of 1 wt. % to 5 wt % of diuron in the copper oxide biocide coating system has further increase the surface glossiness and hence improves the antifouling properties for the coating system.

In this work, the glossiness test was conducted to study the surface effect with biocide and booster biocide addition in polyester-epoxy binder coating system. From the results, higher percentage of pigment volume concentration (PVC) of copper oxide biocide has decreased the glossiness unit of the coating system. For both locations in Lumut and Penang Island, the value of gloss unit decreased with immersion in seawater for 30 days. This may be due to the increase of biocidal leachates from the coating into the seawater. However, in the booster biocide coating system, the gloss unit was observed to increase as the concentration of diuron is increased. The addition of diuron also shows an increased in the gloss unit after 30 days of immersion in seawater as compared to earlier biocide system without diuron. This observation shows that the appearance of the coated surface has been improved with addition of diuron and thus gives the better antifouling properties of the antifouling coating system.

The surface morphology of the copper oxide and copper oxide-diuron coating system has been analysed using SEM at room temperature. The effect of adding different compositions of copper oxide has brought to the changes the surface morphology of the coating systems prepared. The addition of diuron as booster biocide has proven that it can be one of the settlements of biofouling as it can increase the surface smoothness and improves the surface roughness of the coated panels. Overall results also show that the antifouling performance is related to the release of biocidal species. The release of copper oxide helps to prevent the microorganism in seawater to adhere on the coatings. The addition of diuron has further enhanced the appearance of the coated surface by reducing the chalking effect and hence increased the antifouling surface effect.

Suggestions for Further Work

For further work, the coatings can be improved by adding filler or composite material which can increase the coating resistance for longer period of time which will

promotes better adhesion of the coating to the substrate and hence better anticorrosion effect. The antimicrobial effect of the coated panels also can be studied. Effort should be more put on the controlling the amount of biocides/booster biocides added which will also gives a better antifouling performance. With these, the coatings can be more applicable to reduce the metal leaching that can affect the marine population in the seawater.

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Publications

1. **L. Ismail**, K. Ramesh, B.Vengadaesvaran, S.K.M. Jamari, N.A. Mat Nor, A.K. Arof (2015), "Performance Of Polyester/ Epoxy Binder Coating System – Studies on Coating Resistance, Adhesion and Differential Scanning Calorimetry", *Pigment & Resin Technology*, Vol. 45 Iss: 3, pp.158 - 163 (*ISI/SCOPUS Cited Publication*)
2. N.A. Mat Nor, **L. Ismail**, S.K.M. Jamari, K. Ramesh, B.Vengadaesvaran, A.K. Arof (2014), " Electrochemical Impedance Spectroscopy Study of CuO and Cu Coating Systems", *Pigment & Resin Technology*, Vol. 43 Iss 6 pp. 371 - 378 (*ISI/SCOPUS Cited Publication*)
3. N.A. Mat Nor, **L. Ismail**, S.R. Rau, A.K. Arof (2015), "Studies on Anticorrosion Properties of Polyaniline-TiO₂ Blended with Acrylic-Silicone Coating Using Electrochemical Impedance Spectroscopy", *Pigment & Resin Technology*, Vol. 45 Iss: 1, pp.18 - 23 - (*ISI/SCOPUS Cited Publication*)
4. S.K.M. Jamari, K. Ramesh, N.A. Mat Nor, **L. Ismail**, S.R. Rau, T.S. Ramesh, B. Vengadaesvaran, A.K. Arof (2014), "Acrylic Polyol/Silicone Coating Corrosion Protection Analysis Using Electrochemical Impedance Spectroscopy", *Pigment & Resin Technology*, Vol 44, 1 (*ISI/SCOPUS Cited Publication*)

Presented Papers and Poster Presentations

1. **L.Ismail**, K.Ramesh, and A.K. Arof, "Effects of Copper and Copper Oxide as Biocides in Marine Antifouling Coatings" Presented as Postgraduate Seminar at Physics Qolloquium 2014, 3-4 June 2014, University of Malaya, Kuala Lumpur, Malaysia.
2. **L.Ismail** and A.K. Arof, "Conductivity, Surface Morphology and Dielectric Relaxation Studies of PEO Complexes", Presented as poster presentation at the 4th International Conference on Functional Materials and Devices 2013(ICFMD 2013), 8-11 April 2013, Penang, Malaysia.
3. **L.Ismail**, N.A. Mat Nor, S.K.M. Jamari, K.Ramesh, and A.K. Arof, "Studies on DSC And FTIR of Polyester/ Epoxy Binder System", Presented as poster presentation at the 4th International Conference on Functional Materials and Devices 2013(ICFMD 2013), 8-11 April 2013, Penang, Malaysia.
4. **L.Ismail**, N.A. Mat Nor, S.K.M. Jamari, K.Ramesh, and A.K. Arof, "Evaluation of Corrosion Protection and Water Uptake of Polyester-Epoxy Binder Resin by Electrochemical Impedance Spectroscopy", Presented as poster presentation at the 4th International Conference on Functional Materials and Devices 2013(ICFMD 2013), 8-11 April 2013, Penang, Malaysia