Preparation and characteristic analyses of polymer coatings developed by different organic resins


Centre for Ionics University of Malaya, Physics Department, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia

Abstract

Purpose – Corrosion is an important problem to be taken care in terms of economic and ecological aspects. The aim of this paper is to identify the methods of protection and selection of materials for corrosion protection.

Design/methodology/approach – A novel attempt has been made to formulate a hybrid composite paint system using silicone (S2) and polyester (P3) resins. These resins have been blended in different weight ratios to develop binder for protection coatings. Cross-hatch test, impact resistance test, thermal characterization, impedance measurement and potential-time measurement were conducted on binder coated steel panels. Heat resistance test was carried out using ASTM D2485 standards.

Findings – The results showed that physical and mechanical properties of the coatings have been improved by the addition of silicone into the polyester matrix. The binder system developed using 50 wt per cent polyester and 50 wt per cent silicone showed good physical, mechanical properties and high thermal resistance. The maximum coating resistance of the coatings after 30 days exposure was found to be $9.7 \times 10^5 \Omega$ and the coating can withstand high temperature up to 473 K.

Research limitations/implications – The development of different types of coatings will be useful to achieve higher protection performance. The combinations of different resins and pigments have to be analysed and selected suitable compositions.

Practical implications – The objective of this study is to develop coating system with different resins to achieve better performance and reduce the cost of paint materials. It may be useful for the industries to move forward with new formulation using multicomponent coating materials. A critical combination of the above resins offers better protection for steel structures from high temperature corrosive environments.

Originality/value – The formulation of coating material using two different resins and a single curing agent is a novel approach in this research. This type of research will open new ideas of formulating different coatings using various types of resins. In high temperature corrosion environment, the coatings which is commonly used is silicone based and the price of the raw material is very high therefore to reduce the cost of the raw material, the silicone resin is being blended in different ratios with organic resin to obtain an optimum ratio which can be applied to overcome high temperature corrosion on steel panels.

Keywords Corrosion, Protective coatings, Silicone, Polyester resin, Electrochemical studies, Potential time measurement, Resins

Paper type Research paper

Introduction

A lot of money has been spent annually to control corrosion. Tremendous research has been carried out to find a suitable solution to eradicate corrosion. Protective coatings and cathodic protection methods have been used to prevent corrosion (Wicks et al., 1999; Ananda et al., 2006; Ananda and Sasikumar, 2010). Various materials such as polyesters, epoxy, acrylics, alkyds and silicone have been used for the formulation of coating system (Anand and Alagar, 2004; Erich et al., 2005; Deflorian and Rossi, 2006; Fatemi et al., 2006; Syed Azim et al., 2006; Vengadaesvaran et al., 2010; Ramesh et al., 2007). Recent developments focus on the hybrid composite systems using different organic resins (Raps et al., 2009; Bautista et al., 2011; Rau et al., 2011).

Polyester resin has good physical properties such as good adhesion, scratch resistance and flexibility. Silicone resins have good impact resistance and high thermal stability. This may be attributed to the natural hybrid organic-inorganic structure in silicone molecule (Ramesh et al., 2007). A good coating system must have good physical and mechanical properties to withstand external factors such as abrasion, impact and scratch. It should possess high adhesion power to stick on the substrate. For the application on the hot surfaces the paint system should be able to withstand different temperature levels. Anticorrosion properties must ensure that the coating system should protect the material from adverse exposure conditions. Using a single component resin need to be improved to obtain better performance. There will be way forward to look into using multicomponent to provide excellent properties. This may give several novel ideas to promote research in organic coating industry. The cross-linking method between different polymer molecular structure to develop as coating material in which combinations of two or more polymers can be cross-linked chemically. This is current...
emerging need in coating industry to enhance the performance of the coating materials. The blending of polymers, polyacrylates, polyamide, silicones, epoxies and other organic resins can improve the compatibility, corrosion resistance and mechanical properties with only minor changes in their important properties as compared to pure resin (Erich et al., 2005; Syed Azim et al., 2006; Raps et al., 2009; Selvaraj et al., 2009; Niu et al., 2010; Bautista et al., 2011). Among the modifiers elastomers, polydimethylsiloxane, commercially known as silicones is considered as one of the suitable materials for the modification of epoxy/polyester resins, this flexible behavior, such as resistance to weathering and aging, good wetting and film forming ability, low temperature flexibility resulting from Si–O–Si connection and good hydrophobic behavior (Frings et al., 1998; Hinderliter et al., 2006; Miszczzyk and Darowicki, 2003). The hybrid system of silicone polyester is expected to have improved durability, better thermo-mechanical properties, and better corrosion resistance than conventional microbial and coating materials. The present work was focused to improve the thermo-mechanical and corrosion properties of polyester coatings by creating and inter cross-linking network with silicone resin. Keeping all this in mind, silicone and polyester resins have been selected as to formulate the composite binder materials in this study.

### Experimental methods and materials

Silicone resin (S2) and polyester resin (P3) were used to develop binder systems. Silicone resin was supplied by Wacker Silicones, Singapore. The obtained resin was dissolved in xylene to get the required solid content. Polyester resin and polyisocyanate were obtained from Bayer Materials, Malaysia. The resins were taken in different weight ratios (20–80 per cent) and mixed using a mechanical blender. Polyisocyanate acted as a curing agent. Surface treated cold rolled mild steel panels have been used as the substrate in this work. The panels were cleaned with acetone and dried to remove grease and dirt. The panels were then sandblasted to obtain a surface standard SA2.5. The blended binder system was coated by brushing technique on the substrate and allowed to dry at room temperature in a desiccator for a week for further testing procedures.

Coating adhesion to substrate was studied using the cross-hatch method as per ASTM standard D3359 (Niu et al., 2010). A six bladed tool which can make cross-cuts on the coating was used. Damage can be observed on the cuts in terms of flaking or powdering. The mechanical strength in terms of impact resistance was evaluated by Sheen impact tester. A solid weight of 1 kg was dropped from different heights on the coated panels to study the impact resistance of the coating (Selvaraj et al., 2009). Thermal stability of the coating was evaluated by ASTM standard D2485 in which the samples were heated to different temperatures for 24 hours. The surface was then observed for coating failure. Thermal properties were also tested by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Electrochemical impedance spectroscopy (EIS) was used to study coating resistance. EIS analysis is one of the important methods to evaluate the corrosion resistance of paint systems (Deflorian and Rossi, 2006; Hinderliter et al., 2006). In EIS, 3 per cent NaCl solution was taken as electrolyte and the impedance values were noted at regular intervals for 30 days.

In this study, the impedance of polymer composite coatings was measured using HIOKI 3531-01 LCR bridge interfaced with a computer for data acquisition over a frequency range between 42 Hz and 1 MHz with 10 mv constant input. The corrosion protection ability of coatings was studied by potential time measurements (PTM). The samples were immersed in 3 per cent NaCl solution and the potential values were measured for 30 days. From the analyses, the best performing binder system would be identified and TiO₂ pigment added to that binder. Silica and mica were used as extenders. The same characterization methods were used for the paint system.

### Results and discussion

The composite binder systems were formulated using S2 and P3 resins. The average dry film thickness was found to be 100 microns. Table I shows the results obtained from cross-hatch test. Binders containing 30, 40, 50 and 60 per cent S2 have higher adhesion power compared with other systems. Adhesion can also be affected by the stresses (Miszczzyk and Darowicki, 2003) created as the result of solvent evaporation. When the coating is applied on the surface, the functional groups (Wicks et al., 1999; Rau et al., 2011) will make interactions with the substrate surface. Metal substrates normally contain metal oxides or metal hydroxides on the surface. Hydrogen bonding between the functional groups and the metal oxides and/or hydroxides will lead to good adhesion of the coating on the substrate surface (Deflorian and Rossi, 2006).

The impact resistance tests reveal that binders containing 30, 40, 50 and 60 per cent of S2 are able to withstand impact of the intender falling from a 1 m height which is shown in Figure 1. The results show that the increase in the silicone concentration has improved the physical and mechanical properties. However, above a silicone concentration of 60 per cent there was a drop in the impact resistance. This could be due to the over plasticizing effect of S2. The impact was monitored for three weight drop times and average error value was recorded around ±2 per cent.

The coated samples were placed in a furnace and tested for the heat stability at different temperatures. After 24 hours of continuous heating, the binder system containing 50 per cent S2 and 50 per cent P3 did not show any physical changes in terms of color change. It was also free of cracks. This binder material can withstand temperatures up to 473 K for 24 hours. Binders containing 40, 60 and 70 per cent P3 were able to tolerate up to 448 K as shown in Figure 2. The higher heat resistance ability of the coating could have been achieved by the addition of silicone resin with polyester resin with the help of polyisocyanate, there might be cross-linking network formed between the polymer chains. The silicone resin itself

<table>
<thead>
<tr>
<th>Composition S2P3</th>
<th>Adhesion standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:80</td>
<td>3B</td>
</tr>
<tr>
<td>30:70</td>
<td>4B</td>
</tr>
<tr>
<td>40:60</td>
<td>5B</td>
</tr>
<tr>
<td>50:50</td>
<td>5B</td>
</tr>
<tr>
<td>60:40</td>
<td>4B</td>
</tr>
<tr>
<td>70:30</td>
<td>3B</td>
</tr>
<tr>
<td>80:20</td>
<td>2B</td>
</tr>
</tbody>
</table>
has a hybrid organic-inorganic molecular bonding. The addition of hardener with these resins would have enhanced the further molecular interactions and made more Si–C, Si–O–Si functional groups which possess higher thermal stability. The thermal resistance property depreciated when silicone was added more than 50 per cent. This may be due to that the excess of cross-links formed would have been broken into segments.

From EIS results shown in Figure 3, it is observed that the binders with 40 and 50 per cent S2 systems exhibit strong protection against corrosion for the 30 day immersion in 3 per cent NaCl solution and has high coating resistance values around $9.7 \times 10^6 \Omega$.

The coating system behaved completely as insulator to the electrolyte materials. However, at other S2 concentrations the binders have lower corrosion resistance. The uniform formation of the coating on the substrate and the formation of cross-linking network could have influenced the protection ability. The cross-linking network created in the binder system would have covered the surface of the test panels. There could not be any pores for the electrolyte to penetrate. Figure 4 shows the corrosion potential measurement results. The binder with 40 and 50 per cent S2 exhibit higher resistance for the permeation of corrosive medium into the resin coat.

The inability of the molecules of the corroding medium to penetrate the binder system with 40 and 50 per cent S2 may be attributed to the tight and rigid formation of the coating system using these resins and mixed with the hardener.
Cross-linking will increase the network density of the binder system. Polyisocyanate has been employed as the curing agent for the resins. The excess OH groups and NCO groups could have been reacted to make the cross-linking network. Evidence of cross-linking will be manifested by increase in the glass transition temperature (Tg). Tg values corresponding to these samples increased with the increase in silicone content for all the systems.

The Tg values are listed in Table II. The Tg of 100 per cent polyester resin was found to be 301.4 K. But it was increased up to 312.5 K when it was blended with 80 per cent S1 resin. This may be due to the fact that the polymer segments could have been rearranged and new functional groups formed. The increase in Tg values can explain that the cross-linking between the resins has happened and supported by the results obtained by adhesion and impact resistance test methods. TGA showed different stages of weight loss observed. Initial weight loss was due to the evaporation of moisture content and further heating would have degraded uncross-linked polymer chains and some functional groups. It can be observed that the thermal degradation of the polyester resin has been delayed by the addition of silicone resin into the matrix.

Table II shows that the per cent residue was higher for the higher silicone concentration in composite matrix. This is attributed to the hydroxyl endgroups interaction between silicone and polyester resins that led to the increase in the network density or it may be due to the formation of silica clusters around the endgroups of the polyesters (Fring et al., 1998). Figure 5 shows scanning electron microscopic images of:

- 40 per cent silicone and 60 per cent polyester binder; and
- 50 per cent silicone and 50 per cent polyester binder system, respectively.

The micrograms show that the coating formation was uniform without any crack. This rigid formation might have helped the coating systems have good characteristic properties.

**Conclusions**

A new hybrid coating system has been developed using silicone and polyester resins and titanium oxide as pigment. Initially, only binder systems were formulated and tested. Various characteristic analyses were conducted to study the performance of the coating. Cross-hatch method and impact resistance method were used to examine the physical and mechanical properties. Binders with 30, 40, 50 and 60 per cent S2 have good adhesion and impact resistance. Binder with 50 per cent S2 and 50 per cent P3 is able to withstand up to a maximum temperature of 473 K for 24 hours. From the PTM and EIS tests, the corrosion resistance ability of the binder materials was evaluated. Binders containing 40 and 50 per cent S2 exhibited very strong protection against corrosion in the 30 days period of immersion in NaCl solution. The binder containing 50 per cent S2 and 50 per cent P3 was chosen as the best performing binder to formulate paint using TiO2 as the pigment. The formulated paint system possesses very high adhesion power, mechanical strength and corrosion resistance for longer period of exposure. The paint can withstand up to 623 K.

<table>
<thead>
<tr>
<th>Composition S2:P3</th>
<th>Tg (K)</th>
<th>% residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>312.8</td>
<td>77.47</td>
</tr>
<tr>
<td>80:20</td>
<td>312.5</td>
<td>73.50</td>
</tr>
<tr>
<td>70:30</td>
<td>310.5</td>
<td>71.20</td>
</tr>
<tr>
<td>60:40</td>
<td>310.2</td>
<td>63.03</td>
</tr>
<tr>
<td>50:50</td>
<td>309.2</td>
<td>54.67</td>
</tr>
<tr>
<td>40:60</td>
<td>307.5</td>
<td>36.01</td>
</tr>
<tr>
<td>30:70</td>
<td>305.5</td>
<td>28.58</td>
</tr>
<tr>
<td>20:80</td>
<td>305.5</td>
<td>21.16</td>
</tr>
<tr>
<td>0:100</td>
<td>304.4</td>
<td>8.98</td>
</tr>
</tbody>
</table>
Figure 5 SEM micrographs of (a) 60 per cent silicone and 40 per cent polyester; (b) 50 per cent silicone and 50 per cent polyester binder systems

References


Corresponding author

K. Ramesh can be contacted at: rameshkasi@um.edu.my