MODIFICATION OF EPOXY WITH POLYANILINE AND ITS EFFECTS ON CATHODIC DISBONDMENT FACTORS

Noor A’in A. Rahman¹, Mokhtar Che Ismil¹ and Zakaria Man²
¹Centre for Corrosion Research, Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak, Malaysia
²Departmental of Chemical Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak, Malaysia
E-Mail: cucoby@gmail.com

ABSTRACT

The tendency of the external coating of underground pipeline to disbonded is highly due to the service environment. The inadequate coating also becomes one of the contributing factors in the disbonded of an underground pipeline. The function and desired characteristics of an external coating are very important issues. In this work, the performance of Polyaniline (PANI) in epoxy coatings has been investigated by performing the cathodic disbonding test. Varies concentration of PANI was used to find the lowest disbonded radius. The test was carried out at two different conditions for the comparisons purpose. The results were compared with previously stated effects of the potential, time, pH of NS4 soil solution. It was found that the cathodic disbonding radius decreased with increase the PANI content in the epoxy coating system.

Keywords: cathodic disbonding, PANI in epoxy coating, NS4 soil solution.

INTRODUCTION

A severe corrosion damage beneath disbonded of coated underground pipeline is a well-known phenomenon observes worldwide. The combination of external coating and cathodic protection technique are the common practice among pipeline operator to protect them from corrosion. However, the effectiveness of coating is greatly dependent on its ability to resist disbondment around holidays [1]. Disbondment is one of the most common failure modes in pipeline coating while the coating membranes are still highly resistant [2]-[4]. In ideal situations, while coatings isolate the pipe surface from external environments, cathodic protection will protect the pipe at regions where holidays exists in the coating. Holidays are the pinholes and ruptures on a pipe which are caused by a defect in the coating, coating misapplication, and mechanical damage during or after pipeline installation [5]. In reality, at regions where holiday exists in the coating, ground water may penetrate under the coating between the pipe and disbonded coating and initiates corrosion on the pipe surface. Field studies have shown that corrosion under blistered fusion bonded epoxy (FBE) occurred on an 18-inch, 7.9 mm thick, 8.9 km long onshore buried pipeline transporting heavy fuels from the refinery to storage facilities [6]. In addition, considerable research has been done to study corrosion of underground pipelines under disbonded coatings with a defect all over the world. The cathodic disbonding test will provide the information on the performance of the coating system in given electrolyte. More importantly, the synergistically effect between the coating and the applied potential is demonstrated by this test.

A protective coating by Polyaniline (PANI) in epoxy based coating have received more attention in order to reduce the corrosion rate of carbon steel in varies environment. It was claimed that PANI in epoxy coatings is able to resist corrosion in a wide pH range [7]-[11]. A lot of literature are discusses on the protective ability of PANI for different steel and media, but the previous research does not focus the disbondment performance of PANI containing coating in varies pH of the soil solution. This paper describes the preparation of PANI in epoxy coatings system and its ability to resist the disbondment of coating in exposure environment. Resistance to cathodic disbonding is one of the most important properties of pipeline coating during the service. If the coating has a low resistance to cathodic disbonding the likelihood of corrosion and stress corrosion cracking of the substrate steel increase rapidly [12].

EXPERIMENTAL

Metal substrate

The carbon steel substrate was pre-treatment by blast cleaned to Sa 2.5 standard achieve 50 to 55 microns of anchor pattern. Carbon steel of the composition (weight %): C: 0.07, Si: 0.2, Mn: 1.5, P: 0.011, S: 0.003, Mo: 0.02, and iron (Fe) was used in this work. The mixture was then applied by brush in one coat system to a thickness below 200 microns. Dry film thickness (DFT) was measured with coating with the Elcometer 456 coating thickness gauge and was reported in Table-1.

PANI in epoxy coating

PANI in the epoxy coating was prepared using M-xlyndiamine and toluene which act as a cross-linker and solvent respectively. The addition of toluene into the mixtures was increased the solubility percentage of PANI in epoxy resin by more than 90%. Aromatic amine hardeners react with epoxy resins upon mixing to provide films that are extremely resistant to chemicals. PANI in powder form with a particle size range of 0.3 to 100 µm was purchased from Sigma Aldrich. The composition of the prepared coating mixtures is shown in Table-1. A colour change from green to blue (once mix with epoxy) was observed and it was thought that the PANI state was converted from emeraldine salt to emeraldine base which


is more superior in term of corrosion protection ability [13].

Table-1. Coating composition and DFT values.

<table>
<thead>
<tr>
<th>Coating designation</th>
<th>PANI (wt.%)</th>
<th>Epoxy resin (wt.%)</th>
<th>DFT (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP</td>
<td>0</td>
<td>100</td>
<td>153.924</td>
</tr>
<tr>
<td>0.5 EP</td>
<td>0.5</td>
<td>99.5</td>
<td>163.322</td>
</tr>
<tr>
<td>1.0 EP</td>
<td>1.0</td>
<td>99.0</td>
<td>153.162</td>
</tr>
<tr>
<td>1.5 EP</td>
<td>1.5</td>
<td>98.5</td>
<td>173.482</td>
</tr>
</tbody>
</table>

Test electrolyte
The reference solution for the environmental conditions was NS4 soil solution with followed composition (g/L): 0.122 potassium chloride (KCl), 0.483 sodium bicarbonate (NaHCO₃), 0.181 calcium chloride (CaCl₂·2H₂O), and 0.131 magnesium sulfate (MgSO₄·7H₂O). The pH of NS4 soil solution is ranged from pH 8 to 8.5. The solution was made from the analytic grade reagents with distilled water. NS4 solution is widely used as reference solution to simulate the condition under disbonded pipeline coating in many researches [14]–[16]. Hydrochloric acid (HCl) was added to NS4 soil solution to achieve pH 5 and 3 for comparisons purposed. The solution was made from the analytic grade reagents with distilled water.

Cathodic disbonding test
Basic cathodic disbonding test involved with the penetration of the applied coating on the test substrate using a 3 mm diameter drill bit. The test area of the substrate was isolated by the epoxy resin hardener and left about 1.5 cm² of exposed areas. In this particular works, there are two conditions which being study.

Condition A: The substrates were immersed for 24 hours in the different pHs of the NS4 soil solution at 65 ± 1 degrees Celcius (°C) and maintained at a -3.5 volt (V) potential difference. The measured potential was respect to a silver-silver chloride reference electrode (Ag/AgCl) (Figure-1). These parameters are getting from modified ASTM G8 standard. It was also reported that the greatest disbondment occur at 60-65°C [12], [17].

\[ R_{ave} = \frac{R1 + R2 + R3 + R4 + R5 + R6 + R7 + R8}{8} \tag{1} \]

where \( R1 \) to \( R8 \) is the measured disbonded radius of in the radial directions as shown in Figure-2. The standard deviation, \( \sigma \) was given in order to measure how spread out the disbonded radius is. The results were recorded in terms of the area of disbonded coating (in accordance to ASTM G8 [19]).

Condition B: The second condition is at open circuit potential (OCP). The coated substrate has left at 25 °C ± 2 °C for 30 days. Both CD test conditions were run with separate sets of substrates in different NS4 soil solution pHs.

Disbonding analysis
An examination is performed immediately at the end of the test. A sharp thin knife was used to cut a star pattern onto the coated substrate. An attempt was then made to peel easily the disbonded coating from the substrate which delaminated radially outward from the defect site. The extent of the disbonded radius was evaluated by measuring the average disbondment radius, starting from the outside diameter of the artificial defect. Each radius was measured using digital callipers and recorded. The average disbonded radius, \( R_{ave} \) is defined as [18];
RESULTS AND DISCUSSIONS

Figure 3 and 4 shows the pattern of the disbonded area of coated substrate by different concentration of PANI in epoxy based system in both testing conditions. The details of magnitude are listed in Error! Reference source not found.. The average disbonded radius was below than 4 mm for both conditions. Thinning of the coating during testing is caused by chemical attack resulting from electrochemical process driven by the electrical current [20]. Furthermore, the transport of water and ionic species through the coating and dissolution of the oxides are the direct reason for coating delamination in this particular test. Extensive disbonded radius was observed on EP coating system in all pHs for both testing conditions.

In addition, wider disbonded radius of all coating substrates were observed in the presence of the temperature in condition A. Series of 1.5 EP coating system had a lower disbonded radius in all pHs of solution for both conditions. In general, the average disbonded radius increased while decreasing the pH of the NS4 soil solution. In addition, there is not much difference in the performance of 0.5 EP and 1.0 EP especially at condition B. For 0.5 EP, the disbonded radius became similar in all pHs at condition B. The influence of temperature, pH of soil solution and current supplied from both condition were briefly discussed below.

Effect of temperature on cathodic disbonding

In this particular works, it was observed that the disbonded radius is directly proportional to the temperature. A higher temperature will cause a greater expansion of the disbonded radius. In both test conditions, the extensive disbonded radius was observed in condition A compared to condition B.
Table-2. Cathodic disbonding radius in both test conditions.

<table>
<thead>
<tr>
<th>NS4 soil solution pH</th>
<th>Coating designation</th>
<th>$R_{\text{average}}$ (mm)</th>
<th>Standard deviation, $\sigma$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Condition A</td>
<td>Condition B</td>
</tr>
<tr>
<td>pH 8</td>
<td>EP</td>
<td>2.73</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>0.5 EP</td>
<td>2.28</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>1.0 EP</td>
<td>2.27</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>1.5 EP</td>
<td>1.48</td>
<td>1.25</td>
</tr>
<tr>
<td>pH 5</td>
<td>EP</td>
<td>3.89</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>0.5 EP</td>
<td>2.67</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>1.0 EP</td>
<td>2.49</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td>1.5 EP</td>
<td>2.07</td>
<td>1.96</td>
</tr>
<tr>
<td>pH 3</td>
<td>EP</td>
<td>3.93</td>
<td>3.74</td>
</tr>
<tr>
<td></td>
<td>0.5 EP</td>
<td>2.94</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>1.0 EP</td>
<td>2.63</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>1.5 EP</td>
<td>2.15</td>
<td>1.84</td>
</tr>
</tbody>
</table>

The effect of the temperature on the transport of water and ions was not measured by specific experiments. However, higher water vapor pressure increase water vapor permeation through the coating and porosity of the coating grows as a result of thermal expansion [20]. In addition, the dissolution of oxides/coating interface will be accelerated at elevated temperature. The data implied that increasing temperature from 25 °C to 65 °C would increase the disbonded radius of all coated substrates. However, 1.5 EP are able to withstand the increasing of the temperature by showing the lowest disbonded radius among tested coating system in all pHs of the NS4 soil solution.

**Effect of pH on cathodic disbonding**

The lower disbonded radius was observed at pH 8 of NS4 soil solution compared to pH 3 and pH 5 for both testing conditions. Work by K. Saravanan et al. [11] also indicated that PANI in the epoxy coating has better corrosion protection in an alkaline environment. They also claimed that coating containing PANI is able to protect the steel substrate by passivating the exposed area.

The increasing amount of PANI loaded in epoxy coating had provided better corrosion protection against corrosion to the coate substrate. The PANI in epoxy coating is able to improve the neat epoxy performance by providing an effective physical barrier effect against penetration of corrosive ions and protect underlying steel substrate. Therefore, it is believed that PANI in an epoxy coating can provide better protection in alkaline media compare to acidic media.

**Effect of applied potential on cathodic disbonding**

It seems to be generally accepted that the disbonding rate increase with decreasing the electrode potentials [21] which mean polarized the metal with more negatively potential. In this study, condition A has simulated the overprotection condition which becomes one of the factors in increasing the hydrogen evolution reaction on pipeline surface. As a result, the transport of oxygen to the exposed metallic areas becomes the limiting step for the oxygen reduction reaction, allows the hydrogen evolution becomes the dominant reactions at highly cathodic potential [22]. Meanwhile, condition B has simulated the pipeline with lacking of cathodic protection system.

As expected, the available result indicates that the extensive disbonded radius was observed at condition A, which substrate was exposed at applied potential -3500 mV/Ag/AgCl compare to condition B. Our result is in agreement with results published by J. Skar et al. [23] which indicates that disbonding rate of coating increases with more negatively of applied potential. Furthermore, in the presence of PANI in the epoxy coating, the barrier property of the coating is highly improved, especially in the alkaline media. It proves that the coated substrate with PANI in epoxy coating is able to withstand with the negative potential condition compare to neat epoxy.

**Effect of exposure time on cathodic disbonding**

In the literature survey, it is usually said that the disbonded area will increase linearly with time. Steinsmo et al. [24] examined the time dependence of cathodic disbonding test in NaCl solution. They observed an initial time delay period, where disbondment area behaved linearly with time to about 200 days. In this study, the disbonded radius is recorded at the end of the test for both conditions. It is found that the effect of time is not the main contribution for the disbonded radius of the coated substrate in the present study.
disbonding has been demonstrating for a series of PANI

CONCLUSIONS

Effect of various parameters on cathodic disbonding has been demonstrating for a series of PANI content in the epoxy coating. From the presented results it may be concluded that:

- The cathodic disbondment of the coating mainly depends on the temperature and applied potential.
- 1.5 EP is the optimum coating system and attains low disbonded radius compared to the others coating series.
- The coating systems are performed better in alkaline media compared to acidic soil solution media.
- A longer exposure time is recommended to obtain a significant effect by dependence of time.

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REFERENCES


