Acrylic polyol/silicone coating corrosion protection analysis using electrochemical impedance spectroscopy

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Abstract

Purpose – The purpose of this paper is to develop different combinations of acrylic polyol and silicone resins with various weight ratios and to test the coating properties using electrochemical impedance spectroscopy (EIS).

Design/methodology/approach – The performance properties such as coating resistance, capacitance, dielectric constant, water uptake and diffusion coefficient were evaluated using EIS with exposure to 3.5 per cent NaCl solution for 60 days.

Findings – The binders developed in this study were coated on cold rolled steel plates. The dry film thickness was found to be in the range of 50 microns. From EIS results, it was found that Acrylic polyol sample with 30 weight per cent of silicone exhibits the best properties, as it has high coating resistance in the range of 109 Ohms for the full period of exposure, whereas all other samples showed poor performance with the exposure time. For these samples, the parameters measured such as the coating resistance of the samples decreased while the coating capacitance, percentage of water uptake and diffusion coefficient of the samples increased after being exposed to corrosive solution for 60 days. The coatings developed by 0, 10 and 60 weight per cent silicone showed high coating capacitance on the first day of exposure, and these systems failed early during the exposure. The water uptake percentage and diffusion coefficient of all samples were found to be less than 50 per cent and below 10-11 cm² s⁻¹, respectively. An optimum cross-linking between the resins is considered as the main contribution for the best performance shown by the sample that consists of 30 weight per cent of silicone in acrylic matrix that provides maximum barrier properties of the coating.

Originality/value – Developing coatings using hybrid binders (silicone resin and acrylic polyol resin) is new area of research. This will explore more research in the formulation of novel coatings.

Keywords Coating resistance, Dielectric constant, Diffusion coefficient, Double-layer capacitance, Water uptake

Paper type Research paper

Introduction

Electrochemical Impedance Spectroscopy (EIS) is a well-known technique that has been widely used to measure and monitor the corrosion behaviour of organic coatings. By using electrochemistry concept, the electrical resistance of the coatings can be interpreted as the ability of the coatings as a barrier to ions. The data obtained are interpreted by studying the frequency of an applied A.C. wave and often represented by using Randle’s equivalent circuit (Amirudin and Thierry, 1995). Ebrahimi et al. (2012) demonstrated the use of EIS to study the critical pitting temperature of stainless steel and compared it with data obtained from potentiodynamic and potentiostatic techniques. It was found that the charge transfer resistance decreased significantly and also the double-layer capacitance was revealed through EIS method. Al-Muhanna and Habib (2010) stated that the EIS technique is a good method to study the corrosion behaviour of metallic samples under dynamic conditions. Huttunen-Saarivirta et al. (2011) stressed that EIS plays a key role in determining the synthesis conditions for new organic coatings and performances while they are consistent with each other. In this research, we tried to enhance the coating properties of acrylic polyol by mixing it with silicone resin. Acrylic has been known for its high weathering and embrittlement resistance, good mechanical and electrochemical properties and gloss retention (Stoye and Freitag, 1998; Ramesh et al., 2008; Ramesh et al., 2007). These properties could be improved by using silicone resin that has unique chemistry to control liquid/liquid, liquid/solid or liquid/air interfaces (Abidin et al., 2006). Single component acrylic coatings have good physical and mechanical strength and good adhesive property with different types of materials. Pure silicone coatings can be used as antistatic photochromic, antifog, chemical resistance and heat resistant properties coatings (Bernhei, 2006). These coatings are usually applicable to non-metallic surfaces such as plastics.

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To obtain and develop coatings for corrosion protection on metal substrate, there is an attempt made to develop hybrid coatings using silicone and acrylic polyol resins.

Experimental

Acrylic polyol and silicone resins were obtained from Bayer Materials Science and Wacker Silicone, respectively. Mixtures of acrylic polyol (65 per cent solid percentage in xylene) and silicone resin (10 per cent solid percentage in xylene) were prepared in ratios of 100:0 until 40:60. Table I shows the composition of each of the sample. Polyisocyanate (NCO) acts as the hardening agent for these compositions. The substrates used were steel panels, degreased and sandblasted before they were used. The thicknesses of the samples were around 80 × 10^{-4} m. Upon leaving it to dry for a week, the coated panels were tested for the coating properties using EIS. An area of about 5.0 cm² of each sample was exposed to 3.5 per cent of sodium chloride (NaCl) solution that was used as the electrolyte, while saturated calomel electrode and platinum electrode were used as the reference and counter electrodes respectively. The uncoated part of the metal plate was used as the working electrode. The data collection was done by EIS300 software from Gamry Instruments, following ASTM G106. The experiment was conducted for a period of 60 days with the frequency range of 300 kHz until 0.01 Hz at 10 mV rms under open-circuit potential measurement. When an electrolyte diffuses into the coating, it may change the electrical behaviour of the coating while retaining its usual bulk density (Dhoke and Khanna, 2012). All results were taken by analysing the Nyquist and Bode plots obtained from the Gamry Echem Analyst. Information about the coating surface and defects can be analysed at the higher frequency region of the Bode plot, while the lower frequency region gives out details about the activity taken place near the metal surfaces (Dhoke, and Khanna, 2012). Figure 1 shows different Nyquist plots for ideal and delaminated coatings that can be represented in Randle’s equivalent circuit. In this research, the combined effect of acrylic polyol – silicone resins was evaluated by EIS.

Results and discussion

Figures 2 and 3 show the Bode plots of the samples on the first and last day (60th day) of immersion respectively. Some samples exhibited an almost straight-line plot, which was referred to as having capacitive nature, indicating good coatings (Amirudin and Thierry, 1995; McIntyre and Pham, 1996). Initially, there may be interaction of the coating surface and the chloride ion. Such plot is translated as the penetration of electrolyte into the microporosity of the coating. However, no delamination occurs on the surface of the substrate. The surface is considered delaminated which may look like the standard comparison graph as given by (McIntyre and Pham, 1996).

Coating resistance

Coating resistance ($R_c$) or pore resistance is the resistance of the coating resulting from the penetration of charge transport through pores and voids or other defects on the surface of the coating (Amirudin and Thierry, 1995; Zelinka et al., 2009). Figure 4 shows the coating resistance of all samples for the 1st, 30th and 60th days of exposure to 3.5 per cent NaCl. Initially, all samples except A40S60 showed high coating resistances of above $10^8$ Ω. Even after 60 days of exposure, samples with silicone resin in the range of 20 to 50 weight per cent showed good coating resistance (Amirudin and Thierry, 1995), which are above $10^4$ Ω. A70S30 sample showed the best and also the most stable coating resistance values throughout the period of exposure. On the 60th day of exposure the coating resistance of this sample was still at $10^4$ Ω. This could mean that the polymer matrix of acrylic polyol and silicone resin is at the optimum at the ratio of 70:30. Both resins could have cross-linked perfectly at this ratio. A40S60 had fair coating resistance (Greenfield and Scantlebury, 2000) in the range of $10^5$ Ω on the first day of immersion and it has dropped to the range of $10^2$ Ω, A90S10 in which the coating resistance was below $10^4$ Ω after it has been immersed in NaCl for 60 days failed completely. These overall results show that the presence of silicone resin has greatly improve the coating resistance of acrylic polyol except for 4:6 and 9:1 ratios of acrylic polyol to silicone. These may be due to the cross-linking could not be completed since there was not enough acrylic or silicone available in either case. Increase in $R_c$ has been observed during the period of exposure. This could be due to the clogging of corrosion product in the coating pores (Loveday et al., 2004a, 2004b) as observed in A60S40 and A50S50 samples. Therefore, it is suggested to clean the exposed area and change the electrolyte before conducting experiment since the coating resistance is dependent on the resistance of the electrolyte/solution which form conducting pathways (Mekeridis et al., 2012).

Coating capacitance and dielectric constant

By assuming the coating is a medium separating the substrate and the conducting electrolyte both acting as plates, it can be said that the coating itself is a capacitor and thus, the coating capacitance ($C_c$) can be found (Loveday et al., 2004a, 2004b). Coating capacitance and the dielectric constant of the coating ($\varepsilon$) correlated by this equation:

$$C_c = \varepsilon_0 \varepsilon_r A/d$$

where $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-14}$ F/cm); $A$ is the coating area that has been exposed to the electrolyte; $d$ is the thickness of the coating, which is about $80 \times 10^{-4}$ m. By this relationship, it is understood that penetration of water through the coating not only affects the coating capacitance, but also modifies the coating dielectric constant (Bethencourt et al., 2003). In ideal case, $C_c$ is needed solely to fit the data only when a perfect coating acts as a perfect dielectric. But in
In the actual case, the coating will exhibit a time constant $\tau_c = R_c C_c$ as the coating deteriorates (Zelinka et al., 2009; Liu et al., 2003).

Figure 5 shows the dielectric constant of the samples for the days of immersion in NaCl electrolyte. The dielectric constant of all samples increased at the end of the period of immersion as water from the electrolyte enters the samples (Amirudin and Thierry, 1995). As expected, A100S0 that represents pure acrylic polyl had an initial dielectric constant of 2, which is in the range of a typical coating (Loveday et al., 2004a, 2004b). For the whole period of immersion, sample A70S30 had the lowest dielectric constant in the range of 20-25. From these overall results, it can be concluded that at 40 weight per cent of acrylic polyl, the dielectric constant of a mixture of acrylic polyl and silicone is almost to that of water (80) and thus, leading it to exhibit a bad coating performance.

**Water uptake**

When the coated substrates/structures are cleaned with water to remove dust, the coating itself may absorb water. It also may absorb water droplets from its surroundings. Therefore, calculating the amount of water absorbed by a coating is essential. Such situations may cause the coating to swell upon exposure because water tends to gather at low-density locations within the coating (Goossens et al., 2003; Hinderliter et al., 2006). Ulrich et al. (2011) demonstrated the water absorption independent of the salt concentration in acrylic films. It is stated that after a

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**Figure 1** Randle’s equivalent circuit

(a) Ideal coating; (b) delaminated coating
threshold between 30 and 60 per cent of water volume, the coatings start to swell. Similar to dielectric constant of coatings, water uptake or absorption is also relative to coating capacitance (Dhoke and Khanna, 2012). Because the dielectric constant of water is much larger than that of almost all coatings, coating capacitance is used to observe water uptake of coatings because $C_t$ increased with time due to water absorption by the coating (Amirudin and Thierry, 1995; Rammelt and Reinhard, 1992). Brasher and Kingsbury (1954) had derived an empirical equation to calculate water uptake of coatings by taking coating capacitance into account:

$$X_v = \frac{\log(C_t)}{\log(C_o)}$$

where $X_v$ is the volume fraction of water absorbed by the coating; $C_o$ is initial coating capacitance; $C_t$ is coating capacitance at time $t$; and $\varepsilon_w$ is dielectric constant of water (80). Sykes (2004) has made a modification to this equation by introducing dielectric of (dry) polymer, $\varepsilon_p$:

$$X_v = \frac{\log(C_t/\varepsilon_p)}{\log(\varepsilon_w/\varepsilon_p)}$$

However, in this research, the former equation was used because there is only minor difference in values in those two (Bernhei, 2006).

From Figure 6, it can be seen that on the first day of immersion in NaCl, water absorption in all samples is below 5 per cent. An increase in water uptake percentage with time for all samples as shown in the figure almost coincides with the coating capacitance and dielectric constant results. A60S40 had almost constant water uptake percentage up to 30th day. A70S30 maintained the water uptake percentage below 10 per cent and considered to have the best resistance to water absorption. It can be assumed that the interaction between the
hydrophilic groups of the acrylic polyol and silicone with hydrogen bonding from the water is at the minimum since the penetration of water depends on this reaction (Butler et al., 2004). It could also mean that at 70 weight per cent of acrylic polyol due to optimum cross-linking between acrylic and silicone, the pores in the coating are smaller than the diameter of water molecule, thus making it hard for the water molecules to penetrate through the coating (Li et al., 2011).

Double-layer capacitance
A double-layer capacitance only occurs when delamination happens at the surface of the coating. It can be recognized easily when a second time constant $\tau_{dl} = R_{c} C_{dl}$ (Zelinka et al., 2009; Liu et al., 2003) appears at the Nyquist plot such as in Figure 7.

The deteriorated area can be calculated as:

$$A_{dl} = C_{dl}/C_{dl}^0$$

Figure 6 Percentage of water absorption of all samples

Figure 7 Comparison of impedance curve for sample A40S60 for different time intervals

where $C_{dl}$ is the double-layer capacitance of specific area of the uncoated substrate, which is a constant value. However, Amirudin and Thierry, (1995) suggested $C_{dl}$ is more of an electroactive area measurement rather than that of the delaminated area, leading it to depend on the electrochemical state of the surface. The $C_{dl}$ values are usually larger than the values of $C_{c}$ by at least 10 times and like $C_{c}$, $C_{dl}$ also increase with time due to the delamination process (Amirudin and Thierry, 1995; McIntyre and Pham, 1996). Because the value is larger, even a small holiday can clearly be seen in the EIS response. The name “double layer” comes from the separation of a charge on the metal electrode and a charge in the electrolyte by metal electrolyte interface (Loveday et al., 2004a, 2004b).

From Figure 8, it is shown that the double-layer capacitance of most samples increased by at least one magnitude. A70S30 showed no delamination occurred until the end of the experiment, indicated by the zero value of $C_{dl}$. This has supported the coating resistance result which shows A70S30 has the highest $R_c$ value. A90S10 showed the highest $C_{dl}$ which is almost $10^{-4}$ F on the last day of exposure. These increases could be due to the depletion of double layer thickness attributed by the increase of passive layer defects (Ebrahimi et al., 2012). From the 30th to 60th day, A50S50, A60S40 and A80S20 stayed in the range of $10^{-9}$ F which showed the stability of double-layer capacitance of the samples. The inconsistent pattern that appeared in these results could be attributed to the factors explained by Amirudin and Thierry (1995) which stated that this could happened due to irregular distribution of water in polymer coating.

Diffusion coefficient
The transport of water from the surrounding through the coatings has been an important subject in determining the properties of a good protective coating. EIS is said to give off an accurate measurement to determine diffusion coefficient of water because of the separation of interfacial and diffusion process on the frequency scale (Backholm et al., 2008). By assuming that water sorption of the coating obeys Fick’s Second Law:

$$\frac{\partial c(z, t)}{\partial t} = D \frac{\partial^2 c(z, t)}{\partial z^2}$$

Figure 8 Double-layer capacitance of the samples
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where c and D are the concentration and diffusion coefficient of water respectively, it can be used to calculate the diffusion coefficient, D using the water transport solution of the law:

\[
\frac{M_t}{M_s} = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D \pi^2 t}{4L^2}\right)
\]

where \(M_t\) and \(M_s\) represent the mass of water absorbed at time \(t\) and at saturation, respectively, and \(L\) is the coating thickness. This solution is limited to the condition that \(D\) is independent of \(c\) and is applicable to a system desorbing water as well as absorbing water. By taking the water uptake percentage at time \(t\) and at saturation time \(s\) into consideration:

\[
\frac{\log \left( \frac{C_t}{C_0} \right)}{\log \left( \frac{C_s}{C_0} \right)} = \frac{M_t}{M_s}
\]

We can conclude that:

\[
\log \left( \frac{C_t}{C_0} \right) = \sqrt{\frac{4D}{\pi}} \sqrt{t}
\]

where \(d\) is equal to one half of the free film (Perez et al., 1999).

Figure 9 shows the calculated diffusion coefficient of all samples for the immersion period of 60 days. A70S30 shows the least water transport through coating while A90S10 shows the most sorption of water. These results complement the previous results from coating resistance and water uptake.

Conclusions

The important properties of organic coatings such as the coating resistance, dielectric constant, double-layer capacitance, water uptake and diffusion coefficient were studied using EIS technique for samples that were developed using acrylic polyol and silicone resins. All results complement each other. The results show that A70S30 exhibited the best coating properties.

References


This may be attributed to the complete cross-linking between silicone and acrylic resins. The introduction of silicone would have improved the coating properties of acrylic polyol resin with the exception of A40S60 and A90S10. After 60 days of exposure to 3.5 per cent of NaCl, it was found that visibly A70S30 was the only sample that had not corroded. A100S0 and A40S60 samples have corroded severely while others had mild corrosion. This is supported by all the EIS results.
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