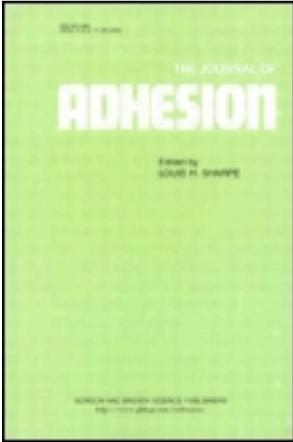


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Studies on the Adhesion and Corrosion Performance of an Acrylic-Epoxy Hybrid Coating

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A hybrid acrylic polyol-epoxy polyol coating cured with aliphatic polyisocyanate has been developed to provide corrosion protection on mild steel panels. Polyisocyanate served as a hardener to initiate crosslinking and as a coupling agent to enhance adhesion of the hybrid polymer resin to the metal surface. The hybrid systems were prepared by blending an acrylic polyol resin (A) with an epoxy polyol resin (E) in various weight ratios and by applying them on pre-treated cold rolled mild steel panels. The dry film thickness was maintained within the range of 40 to 80 μm . The panels were allowed to cure under ambient air condition for 1 week prior to testing. Corrosion resistance and mechanical properties of the coating were studied and characterized. This paper discusses several specific examples on the use of electrochemical impedance spectroscopy (EIS) in the study of coatings in accelerated exposure and the analysis of EIS data from such studies. It is observed that, of the nine coating formulations, one has been found to perform well as an effective and durable hybrid coating.

KEYWORDS *Adhesion; EIS; Hybrid coating; Mild steel panel; Protective coating*

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1. INTRODUCTION

The corrosion of metallic structures can be reduced by organic coatings. The barrier aspect of organic coatings is a key factor in corrosion protection. Under atmospheric condition, water, oxygen, and aggressive ions are the species responsible for the onset of corrosion. Good barrier effects need good adhesion between the coating and the metal substrate. If good adhesion can be established, attack by water at the interface can be prevented [1]. The resistance of a coating system is a general indicator of its performance. For example, coatings with initial resistance above $10^8 \Omega\text{cm}^{-2}$ typically provide excellent corrosion protection while those under $10^6 \Omega\text{cm}^{-2}$ provide poor corrosion protection [2]. The resistance of a coating system generally degrades with time.

This degradation is associated with ion and water penetration into the coating and the subsequent electrochemical reaction at the interface of the coating and metal substrate. Although corrosion control techniques are much diversified in principle, a coating prevents contact between the corrosion agent and the material's surface [3–5].

Wet adhesion, *i.e.*, the ability to maintain adhesion to a metal substrate in the presence of water or electrolyte, was identified as being a very important coating parameter to the performance evaluation of coated metals [6]. Protective coatings such as paint must possess good flexibility; high resistance against impact, chemical, and environment attack; resistance to permeation of moisture; good adhesion; and cohesion. Paints are coating materials that contain binders for good adhesion with the substrate and pigments for colouration. Binders are normally organic materials such as acrylic, polyester, epoxy, and polyurethane resins. These can be blended with each other to obtain enhanced mechanical and electrochemical properties. Surface modifications by chemical means are among efforts to increase adhesion performance of hybrid coating systems. Epoxy-modified acrylic hybrid coating systems can cure under ambient condition without blushing. These hybrid systems exhibit unique performance-to-cost ratio because they can produce hard and chemically resistant films for high performance and even in a salt water environment [7].

The purpose of this study is to facilitate the understanding of the effect on adhesion between hybrid systems of acrylic-epoxy resin and mild steel panels due to water transport property using the non-destructive testing EIS method.

2. EXPERIMENTAL

2.1. Materials

The following chemicals were used for preparation of the hybrid resin system:

- Acrylic polyol resin with 2.9% OH value designated as **A** (Desmophen[®] A365 BA/X – Bayer MaterialScience AG, D-51368 Leverkusen, Germany)

- Aliphatic polyisocyanate resin (NCO) (used as hardener for acrylic polyol resin) (Desmodur[®] N75 MPA/X – Bayer MaterialScience AG, D-51368 Leverkusen, Germany)
- Epoxy resin designated as **E** (NPSN-901X75 Bisphenol-A ~World Wide Resin A.C.R Tech. Co. LTD, Taipei, Taiwan).

2.2. Preparation of Acrylic-Epoxy Hybrid System

In this development, acrylic polyol resin (A) was blended with epoxy resin (E) and polyisocyanate resin was used as a curing agent for the acrylic polyol resin. The proportion of polyisocyanate resin with acrylic resin was maintained at a weight ratio of three (polyisocyanate) to seven (acrylic polyol resin) as specified in the data sheet for acrylic polyol resin. The epoxy resin was dissolved in a known amount of commercial grade xylene. Both polyisocyanate and acrylic polyol resins cure by a combination of xylene solvent evaporation and chemical crosslinking to form films. The above resin mixture and the solvents were mixed in a flat bottom flask and magnetically stirred. By the same preparation method, the acrylic-polyisocyanate-epoxy resins were blended with different blending ratios as shown in Table 1.

The blends (nA:mE) were painted onto the cold rolled mild steel panels sized 0.5 (thickness) × 50.0 (width) × 75.0 mm (length). These steel panels were obtained from steel industries (GT Stainless, Melaka, Malaysia) and the surfaces of the panels were sand-blasted with 60-grit aluminum oxide media at 414 kPa pressure.

The thickness of the coatings was maintained between 40 and 80 μm and determined using a digital Elcometer 456 (Elcometer Instruments Ltd, Manchester, UK) coating thickness gauge model. The coatings were cured under ambient condition of (29 ± 1)°C and relative humidity of 80% for 1 week according to ASTM D1640. The key properties of these hybrid systems were analyzed and investigated for the best performing hybrid ratios.

2.3. Characterization

2.3.1. ADHESION (CROSS-HATCH METHOD)

A Sheen cross-hatch cutter was used in this study [8]. The test method specifies suitable cutting tools with either single or multiple cutting edges. All tests were carried out following ASTM D3359 method B standard. This test method

TABLE 1 Blending Formulation of Acrylic-Epoxy Hybrid System

Acrylic (wt %)	10	20	30	40	50	60	70	80	90	100
Epoxy (wt %)	90	80	70	60	50	40	30	20	10	0
Sample nA:mE	Not cured	20A	30A	40A	50A	60A	70A	80A	90A	100A
		80E	70E	60E	50E	40E	30E	20E	10E	

specifies a procedure for assessing the resistance of the coating system to separation from substrates when a right angle lattice pattern is cut into the coating, penetrating through the substrate. The crossed samples were checked for damages using a digital polarized microscope (Dino-Lite, AM413ZT) (BigC, S.Western Ave, Torrance, CA, USA). These were compared with the standard damage schemes where the classification of 5B indicates the best adhesion while 1B is the worst [9].

2.3.2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

In this study, the EIS measurements for the acrylic-epoxy (AE) coated mild steel panels were performed by using three electrode systems as shown in the schematic diagram in Fig. 2.

An acrylic-epoxy coated mild steel panel acted as the working electrode, a saturated calomel electrode (SCE) (AS 002056 RE-2B, BAS Inc, JAPAN) as the reference electrode, and a platinum electrode (PTE) (OD:6.0 mm, ID: 1.6 mm, BAS Inc, JAPAN) served at the counter electrode. The inner diameter of the polyvinyl chloride tube used was 3.1 cm (tested area is 15.1 cm²) bound to a coated panel with an Araldite[®] adhesive. The inner 15.1 cm² specimen surface was exposed to a 3.5% NaCl solution at ambient condition. This electrochemical cell was placed in a Faraday Cage to reduce current noise picked up by the working electrode and EIS measurements were performed using a Gamry PC14G300 potentiostat and Echem Analyst Version 5.6 analyzer (Gamry Instruments, Warminster, PA, USA). The frequency was in the range of 300 kHz to 10 mHz and the amplitude of the signal was 10 mV. The Bode plot has been used to obtain the coating resistance (R_c) and coating capacitance (C_c) of the samples [10–13]. EIS can be used to determine the adhesion properties of the coating to the substrate by obtaining data from impedance ($\log Z$) versus frequency ($\log \omega$). Capacitance measurements

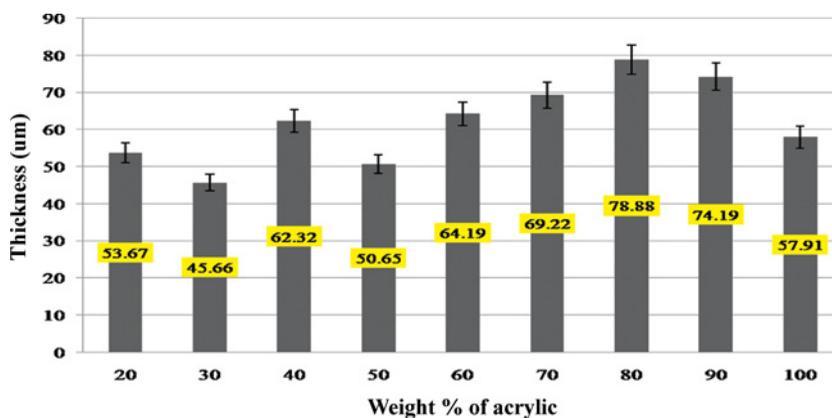


FIGURE 1 Thickness values for acrylic blended with epoxy. (Color figure available online.)

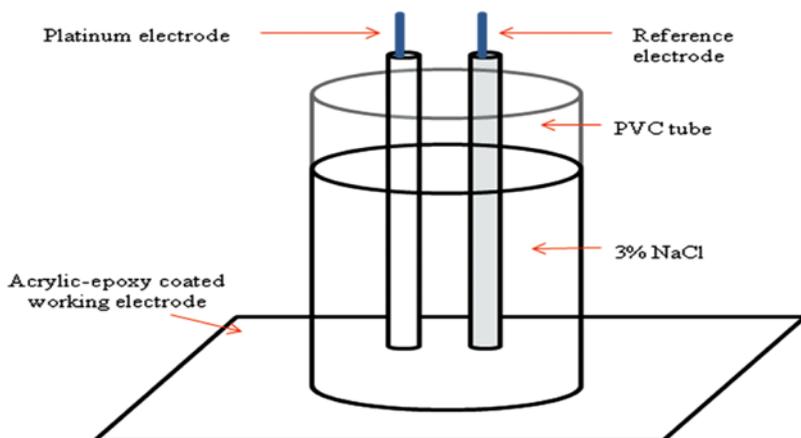


FIGURE 2 Three electrode system used for impedance measurements on acrylic-epoxy coated panels. (Color figure available online.)

can be used to estimate the relative electrolyte uptake rates by the coatings and the rates of delamination of the coating from the metal substrate.

3. RESULTS AND DISCUSSION

3.1. Adhesion (Cross-Hatch Method)

Wet adhesion is an important factor for evaluating the ability of the coating to resist substrate corrosion. The coating system must flow well over the substrate for good intermolecular contact with the substrate to form a coating with thickness between 40 and 80 μm .

Figure 3 represents the degree of adhesion for the various acrylic-epoxy (AE) blends. It is observed that coatings 90% A-10% E and 80% A-20% E have

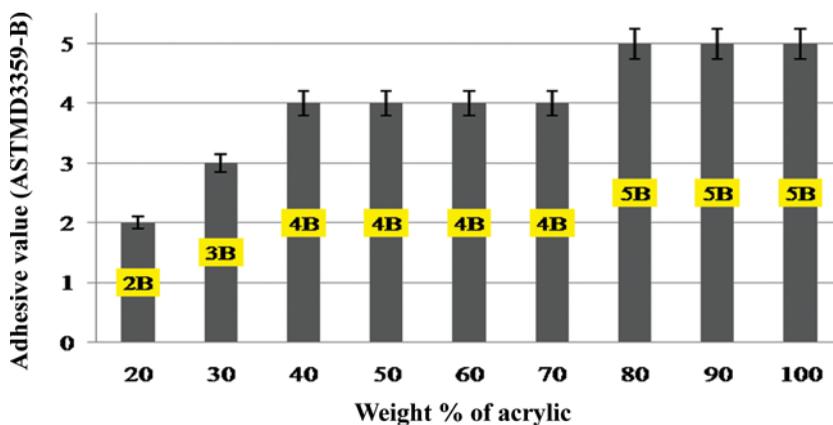


FIGURE 3 Adhesion values for acrylic blending with epoxy. (Color figure available online.)

good adhesion to the substrate compared with the coating from pure acrylic polyol resin. The epoxy resin contributes additional carboxylic and hydroxyl functional groups that together with the functional groups in the acrylic polyol resins form hydrogen bonding with the oxides and hydroxides on the metal substrate. This increases cross-linking and network density resulting in improved adhesion to the substrate [14].

For other compositions 70% A-30% E, 60% A-40% E, 50% A-50% E, and 40% A-60% E, the degree of adhesiveness is lower and the coating can be easily peeled off the substrate as shown in Fig. 4. It may be inferred that increasing E above 20% in the acrylic matrix produces strain in the coating membrane and lowers the resistance to scratch and introduces brittleness due to high cross-link density between acrylic and epoxy functional groups [15].

3.2. Electrochemical Impedance Spectroscopy (EIS)

Impedance data obtained from Bode plots and the equivalent circuit model shown in Fig. 5 describe the behavior of AE coated panels. In this model, R_u is the uncompensated resistance of the electrolyte between the working electrode and reference electrode, C_c is the coating capacitance of the coating, R_p is the pore resistance due to the penetration of electrolyte into the micro pores of the coating, C_{dl} is the double layer capacitance at the delaminated

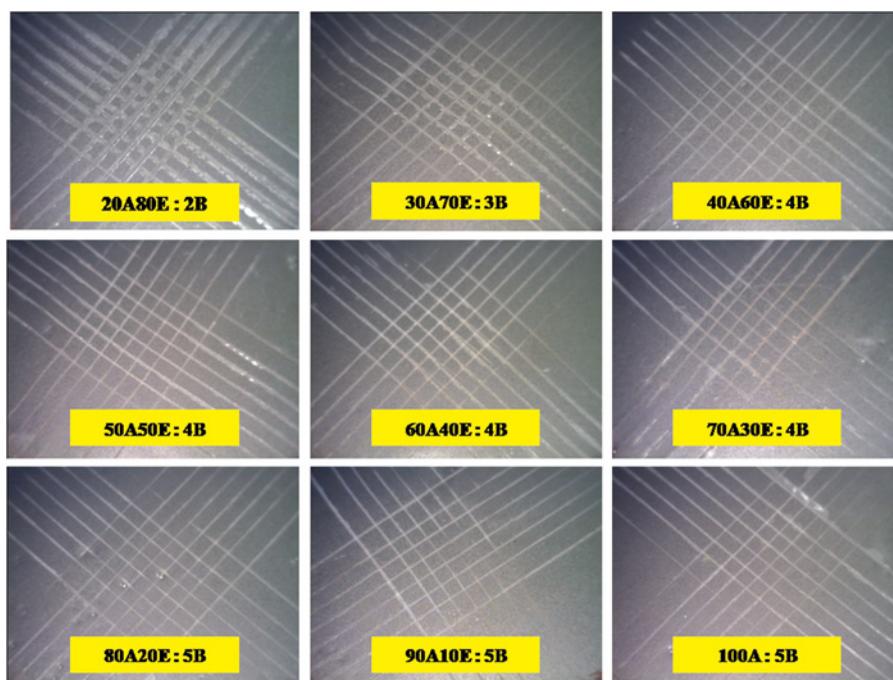


FIGURE 4 Cross cut images of acrylic blended with epoxy. (Color figure available online.)

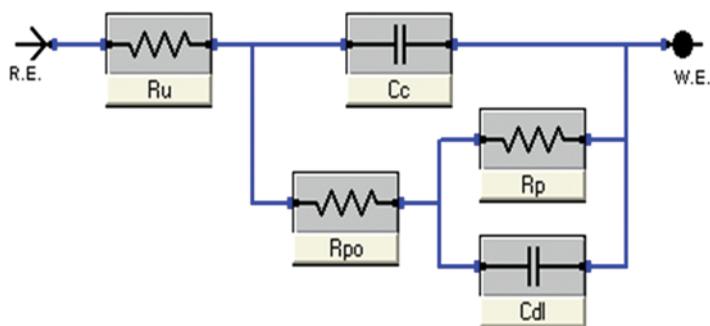


FIGURE 5 Electrical equivalent circuit model: R_u = uncompensated resistance; C_c = coating capacitance; R_p = pore resistance; C_{dl} = double layer capacitance; R_{po} = polarization resistance. (Color figure available online.)

coating/metal interface, and R_{po} is the polarization resistance of the metal substrate electrode.

The value of R_p , C_c , and C_{dl} were fitted by Echem Analyst Version 5.6 software (Gamry Instruments, Warminster, PA, USA) based on the electrochemical circuit in Fig. 5. The variations of R_p with an immersion time of 30 days for different ratios of AE blend are shown in Fig. 6. The sample with 10% E in 90% A shows that the R_p values of the pore resistance is in the order of $10^9 \Omega\text{cm}^{-2}$ up to 30 days of immersion. The high resistance values indicate that the coating is very intact. Higher R_p values above $10^8 \Omega\text{cm}^{-2}$ relate to diffusion barrier of electrolyte *via* the pore. R_p is the ionic resistance of the coating which is inversely proportional to the area of delamination [16]. When the R_p value decreases below $10^6 \Omega\text{cm}^{-2}$, the coating is undergoing a large area of delamination where blister formation and corrosion starts [17,18] which can be observed in all other samples as shown in Fig. 6.

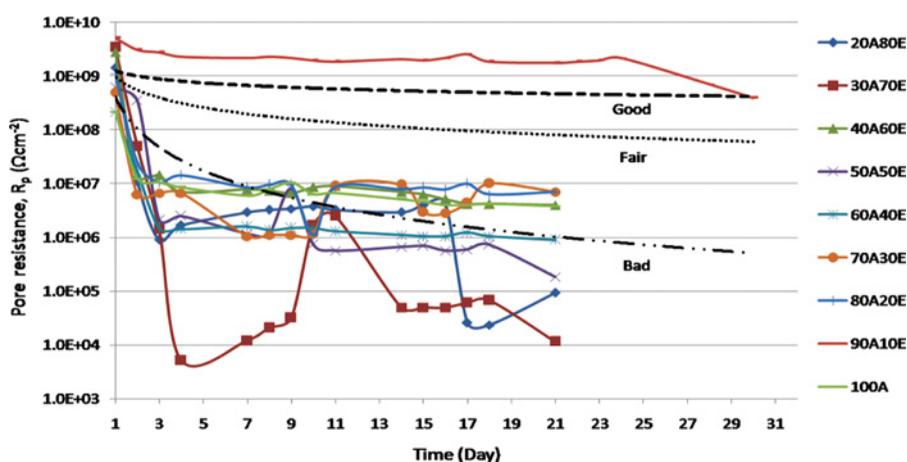


FIGURE 6 Pore resistance (R_p) vs Time of immersion. (Color figure available online.)

The uptake of electrolyte (3% NaCl solution) in organic coatings can be determined directly from capacitance measurements. The evaluation of C_c is shown in Fig. 7. The ion diffusion processes through the coatings can be divided into three phases. In Phase I, upon immersion of coating in electrolyte—ion penetration begins. This leads to a rapid increase in the coating capacitance. In Phase II, the coating is saturated with ions and capacitance remains constant. In Phase III, there is accumulation of electrolyte at the coating-metal interface indicating adhesion loss and possible onset of corrosion [19].

Intact coating adhesion to the metal substrate is indicated by a high R_p value and a low C_c value [20]. All the other AE hybrid systems show the three phase transitions as mentioned above except sample 90A10E. From Fig. 7, it is observed that only sample 90A10E shows a very low coating capacitance that is almost constant for 30 days of immersion time in the 3% NaCl electrolyte. This result supports the destructive adhesion cross-hatch cut test. The continuous increase in C_c is attributed the gradual increase in sodium and chloride ions at the coating-metal interface. This leads to swelling of the coating and loss of its ideal dielectric behavior [21].

Using data from C_c plots, the coating is related to the relative dielectric constant (ϵ) by [22]:

$$C = \frac{\epsilon \epsilon_0 A}{d}, \quad (1)$$

where ϵ_0 is the dielectric constant of free space (8.85×10^{-12} F/m), A (m^2) is the surface area of the coating, and d (m) is the coating thickness. Since the relative dielectric constant of polymers is typically in the range of 3–8, and for pure water is 80 at 25°C, then the uptake of electrolyte will lead to an increase of the dielectric constant and a higher coating capacitance [22].

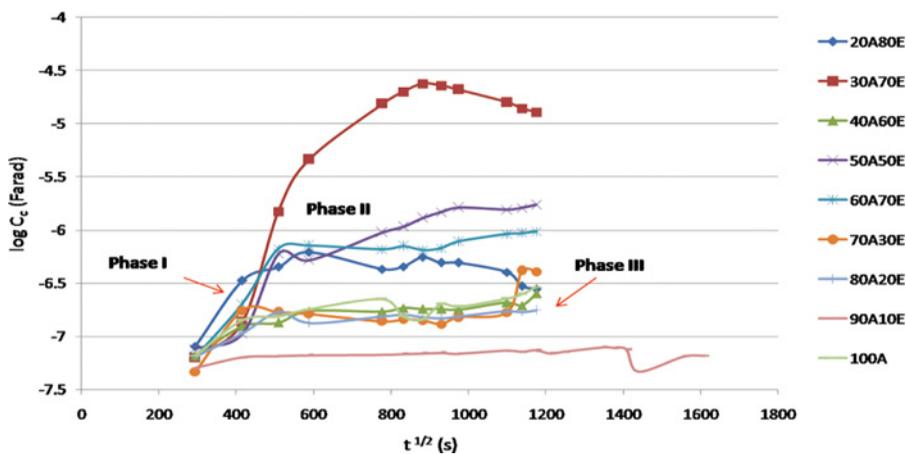


FIGURE 7 Coating capacitance (C_c) vs Time of immersion. (Color figure available online.)

According to Castela and Simoes [22], the dielectric constant of solid, water, and air tri-phase coating is given by

$$\varepsilon = \varepsilon_s \varepsilon_w \varepsilon_a, \quad (2)$$

where ε_s is the solid dielectric constant, ($\varepsilon_w \approx 80$) is the water dielectric constant, and ($\varepsilon_a \approx 1$) is the air-mixed dielectric constant respectively [22]. Dielectric constant ε values are plotted in Fig. 8. It is observed that the 90A10E sample shows a small increase in dielectric constant but within the range of an inert coating system (8–10). This implies that the 90A10E sample exhibits small porosity and possesses good barrier properties.

Other samples show dielectric constant values higher than 10 as shown in Fig. 8, indicating the presence of pores and voids which may lead to electrolyte uptake and transport of ions (Na^+ and Cl^-) at the coating-metal interface. Volume fraction of water, φ_w , is calculated from the equation [22,23]

$$\varphi_w = \frac{\log\left(\frac{C_t}{C_o}\right)}{\log \varepsilon_w}, \quad (3)$$

where C_t is the capacitance at instant t and C_o is usually obtained by extrapolating the coating capacitance to $t=0$ [22,23]. When φ_w increases, ε increases, resulting in higher capacitance. φ_w for AE hybrid coating is presented in Fig. 9.

Only sample 90A10E has a low water absorption at the saturation stage. Also, as seen in Fig. 6, the 90A10E sample becomes saturated leading to a

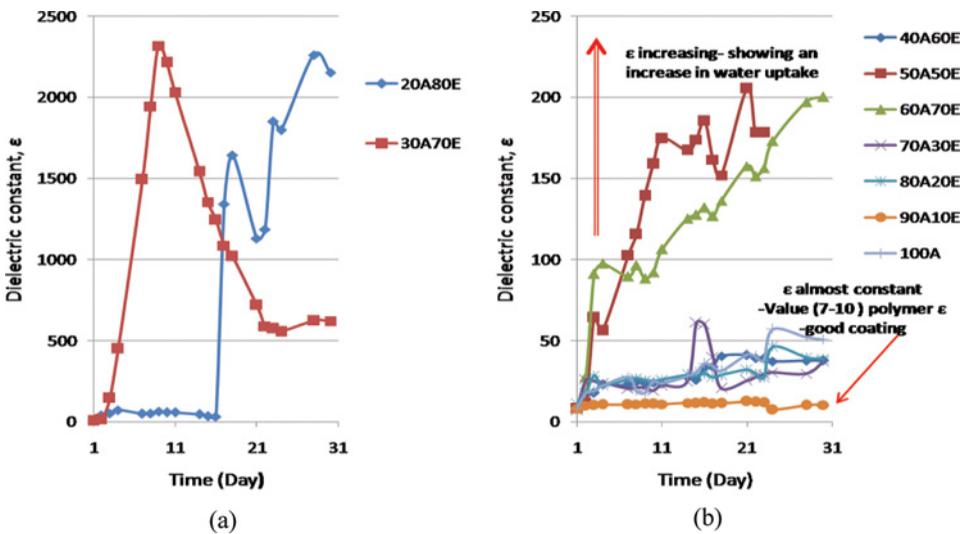


FIGURE 8 Dielectric constant (ε) vs Time of immersion. (Color figure available online.)

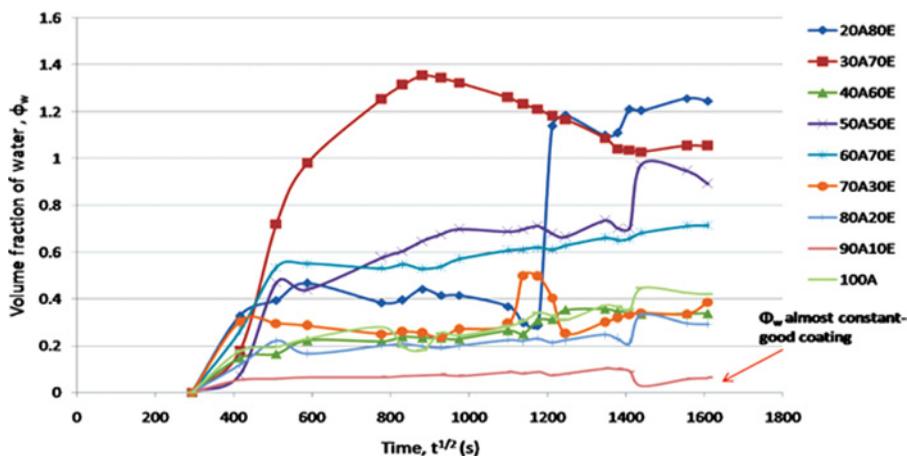


FIGURE 9 Volume fraction of water (ϕ_w) vs Time of immersion. (Color figure available online.)

plateau where the capacitance remains constant, indicating better barrier properties. As a consequence, the observed changes in the capacitance are linearly related to the water uptake. However, after the saturation of the coating has been reached, coating capacitance continues to increase slowly. This phenomenon may be due to different electrolyte uptake rate or due to disbonding of the hybrid coating which depends on hydroxide ion generation at the coating and metal interface [24].

4. CONCLUSION

In this paper, the adhesion and EIS techniques were used to evaluate the performance and critical properties of nine hybrid AE coatings under laboratory corrosive environments. Interfacial integrity plays a major role in the barrier performance of the coatings. This defines the adhesion strength of the coating to its substrates. A hybrid system which forms compatible blends with an epoxy resin was developed. It is observed that the cross-hatch method and the EIS technique reveals the adhesive strength of acrylic-epoxy hybrid coatings in ambient conditions. EIS is well-suited for quantitative evaluation using equivalent circuit elements that enable to one follow the main mechanism of coating protective properties in terms of water uptake, diffusion, and electrical conduction through the coating. The hybrid coating comprising 90% acrylic resin blended with 10% epoxy resin exhibits good adhesion properties. EIS data shows significant differences between samples. Only the 90A10E sample exhibits an excellent barrier protective property such as R_p above $10^7 \Omega\text{cm}^{-2}$, C_c below 10^{-7} F, and ε in the range of 8–10 up to 30 days of immersion time in 3% aqueous NaCl. This sample also has a lower volume

fraction of water due to the prevention by the coating of ions, water, and oxygen molecules from reaching the substrate. The incorporation of epoxy resin (10%) gives an improvement in the coating resistance and in the adhesion performance of the acrylic resin.

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