Studies on Electrochemical Properties and FTIR analysis of Epoxy Polyester Hybrid Coating System

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Electrochemical impedance spectroscopy (EIS) studies have been carried out to characterize the corrosion properties of polyester-epoxy coating systems. The results showed that sample contained 90% of polyester (90P10E) obtained the excellent corrosion performance from the beginning until the end of exposure time. The highest corrosion values obtained on the 30th day was found to be 7.094 x 10^{11} Ω with lower double layer capacitance of 5.312 x 10^{-19} Farad gained by samples of 90% polyester. Moreover, the water uptake and dielectric constant were the lowest at the end of exposure which were 0.369 and 1.020 x 10^{-10} respectively, indicating that the sample has good corrosion protection capabilities. FTIR analysis determined the functional groups and cross-linking occurred in the coating samples and supporting the adhesion between the resins as well as with the substrate.

1. INTRODUCTION

Steel plays an important part in the development of modern world. Heavy constructions such as marine, chemical and petrochemical industries use steel as the major construction materials. Protection of steel structure from corrosion by organic coatings is well known practice. The barrier effect of organic coatings is a key factor in the corrosion protection provided to the substrate. Under atmospheric exposure, water, oxygen and aggressive ions are the element responsible for initiating the corrosion processes [1]. The resistance of coatings decreases by corrosion process. The prediction of the corrosion resistance of the steel is relevant in the assessment of the quality of such materials frequently used in industrial applications and it may give indication of whether the organic coating is protective or not. There are several ways to examine corrosion phenomenon. In recent years, the use of

Electrochemical impedance spectroscopy (EIS) for investigation of corrosion has increased rapidly and this approach is used widely in studies of corrosion prevention by organic coatings [1,2,3]. EIS is based on surface impedance determination and is of outmost importance for controlling the integrity and quality of organic coatings [4]. EIS has proven to be a valuable test method for the electrochemical characterization of the protective organic coating. The qualitative and quantitative data can be obtained from EIS using applied signal wave via three electrodes known as working electrode (WE), counter electrode (CE) and reference electrode (RE) [3,5]. The applied current passes through WE and CE while potential is taken between RE and WE. In this study, the polyester-epoxy hybrid system coated on mild steel panels were measured its corrosion behavior using EIS measurements. The aim of this research work is to analyse the coating behavior in corrosion environment as well as to study adhesive bonding formation between the coating constituents and with the metal substrate.

2. EXPERIMENTAL SETUP

2.1 Sample preparation

Two types of resin were used to form hybrid coating systems which are polyester and epoxy resins. The polyester resin was obtained from Bayer Material Science while the epoxy resin was purchased from Nan Ya Plastics Corporation. Both of the resins were mixed together and dissolved in xylene solution. Different hybrid coating systems were prepared by varying the weight percentage of polyester and epoxy resin ratios as presented in Table 1. The different hybrid systems were then mixed with polyisocyanate (NCO) which act as hardener for polyester [6] since it cannot cross-link without the addition of NCO. The polyisocyanate used was Desmodur type of Bayer Material Science. The amounts of NCO added were calculated based on below equation:

$$NCO = \frac{2.47 \ \times \ \%OH \ of \ acrylic}{\%NCO} \ \times \ amount \ of \ polyester \ (g) \qquad \text{Eq. (1)}$$

Table 1. Coding of hybrid polyester-epoxy coating systems

Polyester (%)	Epoxy (%)	Code
100	0	100P
90	10	90P10E
80	20	80P20E
70	30	70P30E
60	40	60P40E
50	50	50P50E
40	60	40P60E
30	70	30P70E

All test panels used in this study were mild steel panels. A surface treatment was applied on the samples by solvent degreasing to remove the presence of grease and dust before being sandblasted using sand grains. The hybrid coating systems were then sprayed on the steel panels using spray coater. The coated steel panels were then placed in a room temperature for a week until the solvent have completely evaporated and cured before proceeding for corrosion resistance test. After one week, the thicknesses of the coated panels were measured using an Elcometer thickness instrument; the coated panel thicknesses was about 30 μm.

2.2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is the method in which the impedance of an electrochemical system is studied as a function of the frequency of an applied a.c. wave. Electrochemical impedance spectroscopy (EIS) has been successfully applied to the study of corrosion systems and has been proven to be a powerful and accurate method for measuring corrosion rates. EIS is based on surface impedance determination and is of outmost importance for controlling the integrity and quality of organic coatings [4]. The corrosion performance of organic coatings has been widely researched via electrochemical impedance spectroscopy (EIS). Data collected via impedance techniques can be analyzed by modeling the data on known equivalent circuit which is a standard tool for the interpretation of impedance data suing Bode plot. The circuits, Fig 1 which are used to model this type of data are usually comprised of R_s, the solution resistance, followed by a coating capacitance C_c in parallel with R_p or R_c, the pore/coating resistance. An element called C_{dl} (double layer capacitance) is also included in parallel with R_{ct} (charge transfer resistance) in corroding coated metals. The coating capacitance C_c is usually plotted as a function of the immersion time in solution, which increases with the uptake of water into the coating. The double layer capacitance C_{dl} represents the wet area under the coating, which is the area in contact with the electrolyte. It is primarily affected by surface roughness, surface oxidation, accurate measurement of this parameter is easily performed using EIS giving an indication of any delamination which is taking place. The pore/coating resistance R_c relates to the diffusion of electrolyte through the organic coating via the pore, which can affect the barrier properties of the coating; the parameter R_p is the ionic resistance of the coating which is inversely proportional to the area of surface defects (pores) [3,5]. For systems in immersion, the water content also can be determined by electrochemical impedance. Capacitance measurements were used to calculate the amount of water penetrates through the coating layer. The water uptake (Ø) of the coating was determined by below equation:

$$\text{Water uptake } (\emptyset) = \frac{\log (C_t/C_0)}{\log \varepsilon_w} \qquad\qquad \text{Eq. (2)}$$

where C_t and C_0 are the values of the capacitance at time t and time 0, respectively, and ε_w is the dielectric constant of water = 80 at 20°C.

Capacitance measurements (C) were not just use for the water uptake calculation but also can be used in calculating the uptake of ions into the coating layer. This is because during the exposure

time, there were also ions exchange process takes place. The higher the number of ions, the higher the dielectric constant (ε) of the coating which can be calculated by given equation:

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$ Eq. (3)

where ε_0 is the dielectric constant of free space (8.854 x 10^{-12} F/cm), A the surface area of the coating and d is the coating thickness.

Bacon et. al, [7] have measured the resistance of over 300 coating systems and determined a direct correlation between the resistance as well as the ability of the coating to protect the underlying steel from corrosion. Three general classifications, based on a sustained resistance values, were established during this investigation: good, fair and poor [5,8,9 and10].

Most coatings have resistances of about Log R = 9 ohm cm^{-2} at the beginning of immersion, followed by a decrease with the length of time. A coating that maintains a resistance of 10^8 ohm cm^{-2} have good corrosion protection capability whereas those with resistance below 10^6 ohm cm^{-2} will be classified as poor coatings [8,9]. EIS was conducted using a three electrode system. The coated panel area exposed to the electrolyte solution of approximately 5 cm^2, served as the working electrode. Saturated calomel electrode was used as reference electrode while the counter electrode was platinum electrode. The measurement was conducted at room temperature in 3.5% NaCl solutions immersion up to 30 days of exposure. The a.c. impedance measurement was performed at the open circuit potential using a signal wave of 10 mV amplitude with frequencies varied from 300 kHz to 0.01 mHz using Gamry Instruments EIS G300. All results were taken by analyzing the Bode plots obtained from the Gamry Data Analyst. Higher frequency region of the Bode plot contained information regarding the coating surface while the lower frequency regions include the information on the reaction happen near the metal surface. The ideal and delaminated coating can be observed in Bode plots [10].

2.3 Fourier Transform-Infared Spectroscopy (FTIR)

FTIR determined the identifications of functional groups and cross-linking occur in compounds. The FTIR analysis spectra were recorded in the transmittance mode using ATR-Nicolet iS10 Spectrometer (Thermo Fisher Scientific Inc.) by using deuterated triglycine sulphate KBr method for the measurements. For all the spectra recorded, the samples undergoing a 32-scan data accumulation in the range of 400-4000 cm^{-1} at a spectral resolution of 4.0 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Impedance Spectroscopy (EIS)

Fig. 1 and 2 show the Bode plots of coating system on the 1st and 30th days of immersion. The Bode plots were analyzed to evaluate the corrosion performance of coating in terms of coating resistance, capacitance double layer, water uptake and dielectric constant. In the measurements of the impedance, the coating performance properties were expressed in different parameters such as R_s, R_c,

C_c and C_{dl}. Fig. 3 shows the effect of hybrid polyester-epoxy system on coating resistance after immersion into 3.5% NaCl solution up to 30 days of exposure. It is evidence that the 90P10E has a higher ohmic resistance.
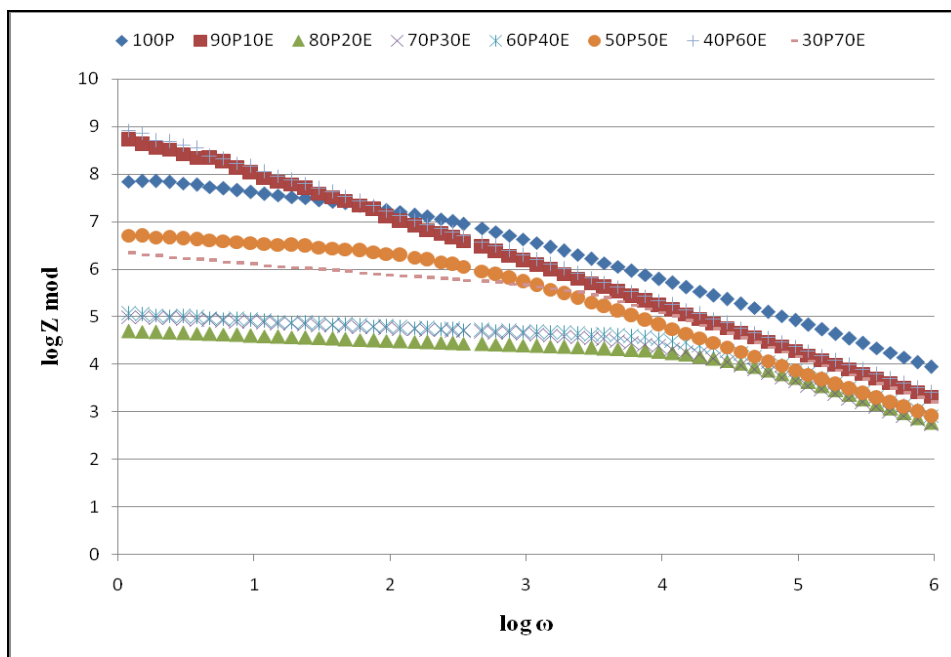

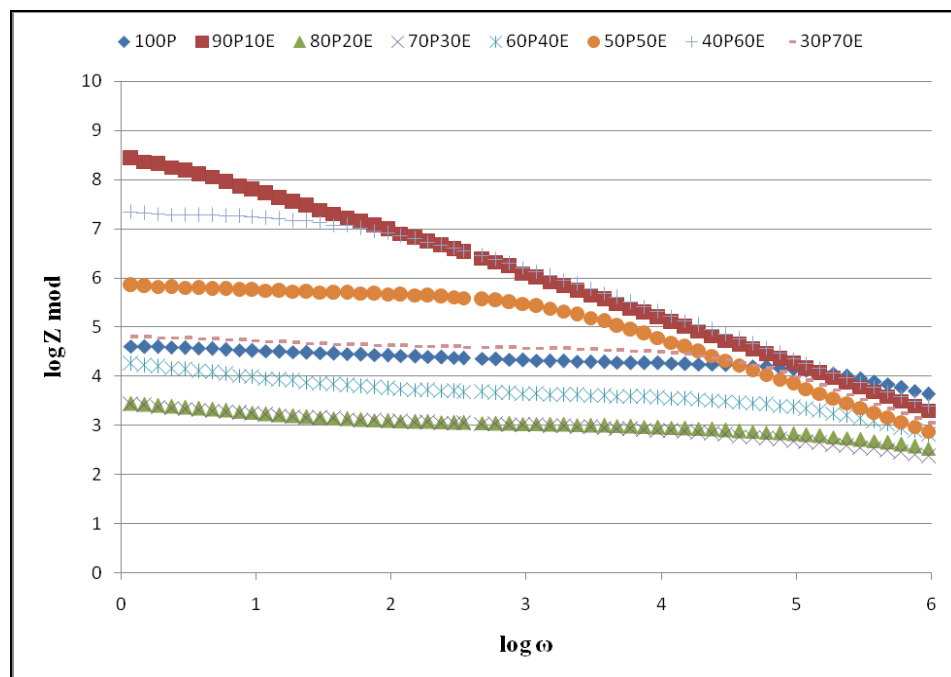**Figure 1.** Bode magnitude plot for polyester-epoxy coating systems on 1st day of immersion in 3.5% NaCl

Figure 2. Bode magnitude plot for polyester-epoxy coating systems on 30th day of immersion in 3.5% NaCl
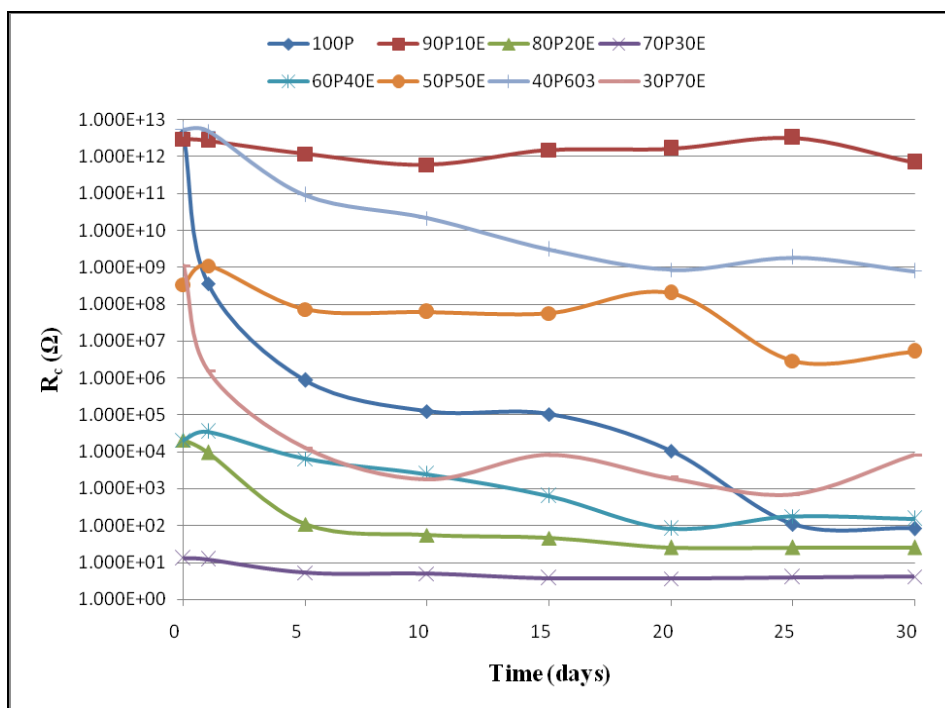
Figure 3. Graph of coating resistance (R_c) of the coating samples during 30 days of immersion in 3.5% NaCl

The coating resistance of the sample was found to be in the range of 10^{12} ohm cm^{-2} throughout the time of exposure and towards the end of exposure the values was highest which 7.094 x 10^{11} ohm cm^{-2}. The coating resistance show little changes, this is possibly due to the uniformity of cross-linking [2]. The hybrid coatings of 50P50E and 40P60E also have good protection capabilities since both of the coating system still gained coating resistance higher than 10^6 ohm cm^{-2} up to 30 days of immersion [8]. Meanwhile, coating resistance of the other samples were lower since beginning and drastically decreased with increasing immersion time (30 days) which the coating resistance below the 10^5 ohm cm^{-2}. The lowest coating resistance achieved by samples of 70P30E which gained coating resistance of below 10^1 ohm cm^{-2} almost the whole time of immersion. It is considered that a decrease in the coating resistance value may be due to the penetration of water and movement of ionic species through the coating layer, increasing the coating conductivity. Initially, the electrolyte penetrates through the coating layer, and sets up the conducting paths at different depths within the coating [2,9]. Moreover, the penetration is completed and the electrolyte phase meets the panel and a corrosion cell is activated. The barrier properties of the hybrid coating decreased with increasing of immersion time resulting an increase in corrosion rate, possibly through the presence of pores in the coating or an increase in the area exposed at the existing pores. However, with increasing of exposure time (towards 30 days), a further increase in the coating resistance was observed (for samples of 50P50E and 30P70E), suggesting that pores within the coating layer were blocked with corrosion products, and ionic movement in the coating layer was lowered [11]. With further time, the coating resistance will continuously decrease, again suggesting that the reason also due to the increase in corrosion rate as the result of pore generation in the coating layers.
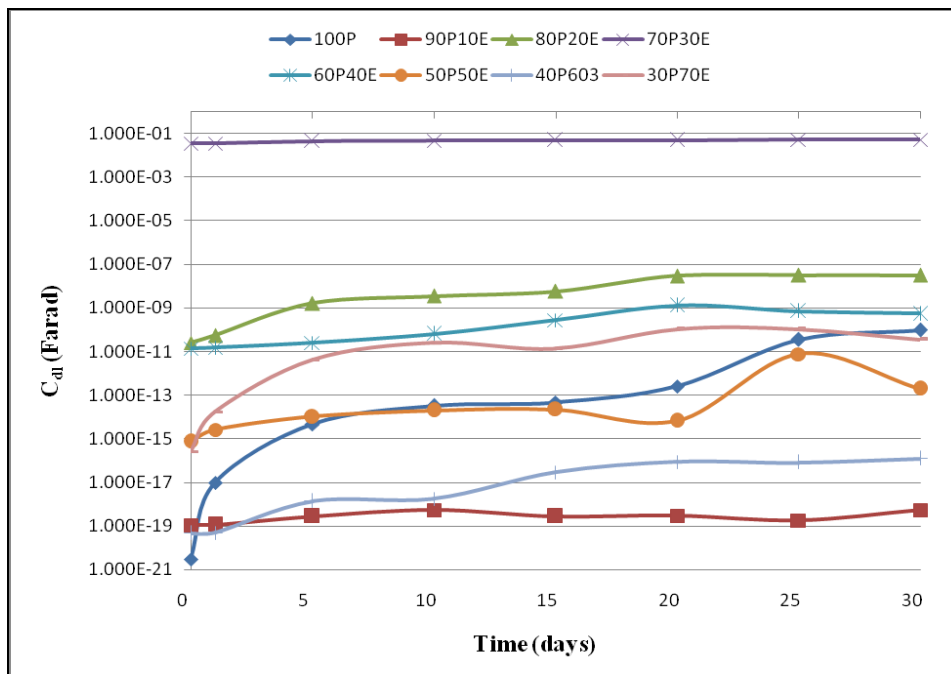
Figure 4. Graph of double layer capacitance (C_{dl}) of the coating samples during 30 days of immersion in 3.5% NaCl
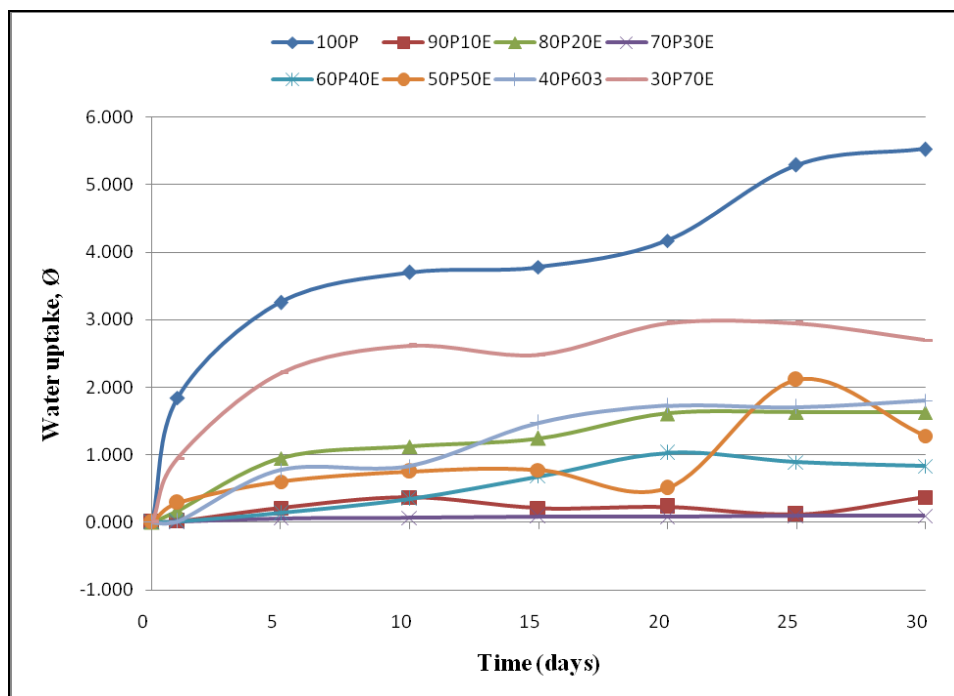

Figure 5. Graph of water uptake (Ø) of the coating samples during 30 days of immersion in 3.5% NaCl

Fig. 4 shows the double layer capacitance (C_{dl}) of the organic coating systems, which is related to the area of the substrate in contact with the electrolyte because of loss of adhesion, increases with increasing of immersion time. Obviously, it can be revealed that the samples of 90P10E contributed to

the lowest C_{dl} values compared to the other samples while samples of 70P30E gained highest C_{dl} values towards 30 days of immersion. At the 30th days of immersion, the C_{dl} values of 90P10E sample was 3.565×10^{-11} Farad while 5.305×10^{-02} Farad for samples of 70P30E. High performance systems show low double layer capacitance. The higher the double layer capacitance, the higher the disbonded area, means that there are increases in corroded area under the coating as a consequence of progressive degradation. Many factors can lead to the increase of this double layer capacitance. Factors such as pressure of the corrosion products on the organic coating and a chemical or electrochemical gradient across the coating which can increase the number of the defects in the systems and reduces the coating resistance can also increase the double layer capacitance [12]. The water uptake in organic coatings can be determined directly from the capacitance measurements. The coating capacitance values will increase due to water uptake which may arise from water accumulation beneath the coating. Fig. 5 presents the polyester-epoxy hybrid coating water uptake during 30th days of immersion in 3.5% NaCl. It is clearly shown that sample of 100P contributed to the highest water uptake from the beginning and keep increasing until the end of immersion, indicating that the absorption and saturation of water in the coating is higher.
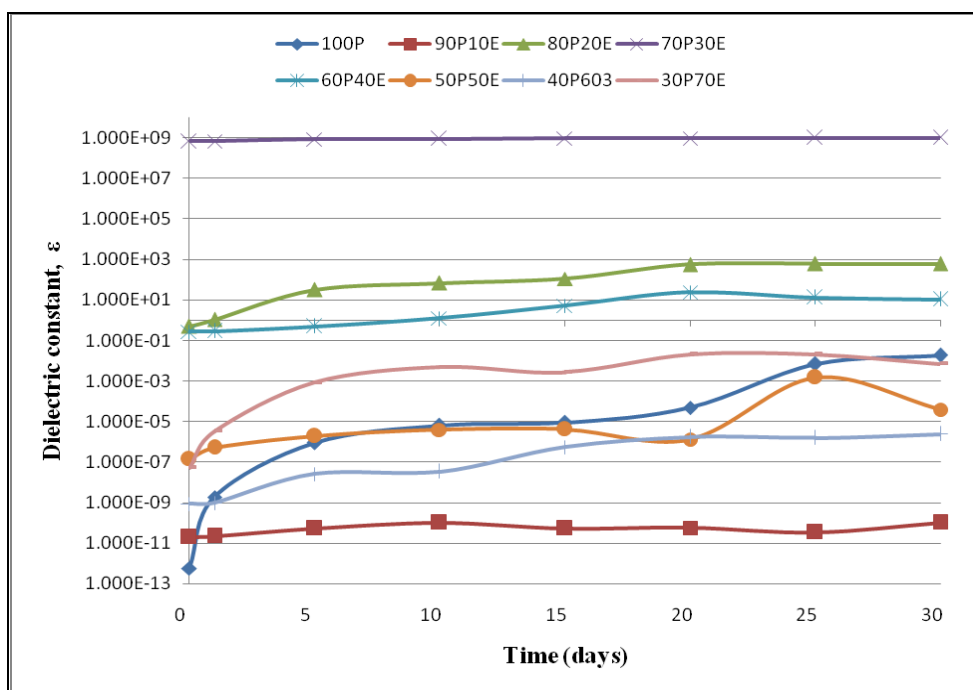

Figure 6. Graph of dielectric constant (ε) of the coating samples during 30 days of immersion in 3.5% NaCl

Meanwhile, the samples of higher resistance 90P10E achieved in low water uptake approximately 0.369 for the whole time exposure, followed by sample of lower resistance 70P30E. There are two factors may affect the water permeation through the coating [13], the crystallinity and the chain stiffness of the coating; both of these act to decrease the diffusion rate as they increase. Thus, the samples of lower water permeation (90P10E and 70P30E) experienced this kind of situation which leads to lower absorption of water into coating. However, the capacitance measurements were

accounting not just for the water, but also for the uptake of chloride ions, and for the reorientation of the mode of distribution of water within the coating [14]. The process of degradation of a polymer coating during immersion occurs in several stages. First, water and ions penetrate into the coating, but the electrolyte penetrates preferentially in the areas with lower cross-linking density. Ion exchange processes were then take place, in which the ions from the electrolyte become attached to the polymer network.

This results in decreasing of coating resistance which lead to diminish of protective capability of coating [15]. The uptake of ions from solution seems to be more predominant factor for this problem. The higher the number ions the higher the dielectric constant of the coating and since the capacitance is proportional to the dielectric constant, the higher values of the capacitance. Fig. 6 showed the dielectric constant of the samples during immersion time. Data revealed that for the whole time exposure (up to 30 days) the lowest coating resistance 70P30E, contributed to the highest dielectric constants (in the range of 10^9) indicating the highest uptake of ions (saturation of the coating layer with ions), which lead to the corrosion production. Sample of high performance resistance 90P10E achieved the lowest uptake of ions (lower ion penetration) in the range of 1.020×10^{-10}, which lead to the lowest dielectric constant values. This indicates that the 90P10E sample exhibits small porosity and possess good barrier properties. The coatings with high resistance and lower resistance have not shown complete delamination or peel off from the substrate. This shows that there would be strong adhesion bonding between the metal substrate and the coating components. This may be a reason, and then when the formations of pores in the coating grow, the rate of corrosion and reduction in resistance reduces.

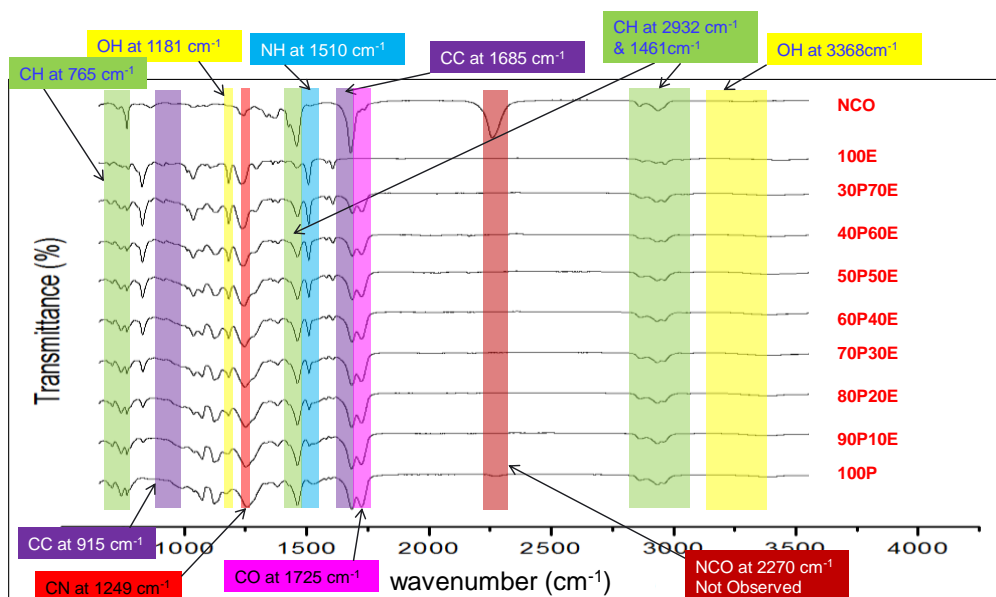## 3.2 Fourier Transform-Infrared Spectroscopy (FTIR)

Figure 7. FTIR transmittance spectrum of polyester blended with epoxy resin

Fig. 7 shows the FTIR spectra of all the binder systems. There were shifts in the peaks of the functional groups which can explain cross-linking occurs between the resins. Fig. 7 depicts the FTIR spectra for the polyester-epoxy blends from 500 to 4000 cm^{-1}. There were evidence that crosslinking between polyester and epoxy resins confirmed occur due to the existence of the stretching asymmetrical C-C band and contraction of the C-O band [16,17]. This band was not observed in the pure epoxy sample (100E), but observed in all samples containing polyester-epoxy resin. In pure polyester sample (100P), the C-N band is observed at 1258 cm^{-1}. However, as the concentration of epoxy increases in the polyester-epoxy matrix, there were prominent band shift observed at 1249 cm^{-1} as shown in Fig. 7. According to the Rau et al., [16], the shift is related to the asymmetrical -C-O-C-stretching of aryl alkyl ether of epoxy. There was also sharp peak in the epoxy resins spectrum observed at 1181 cm^{-1} which attributed to ether linkages. The C-O band was observed at 1173 cm^{-1} shift to 1181 cm^{-1}, confirming that there were formation of a polymer network between polyester and epoxy in the binder systems. In this binder systems, polyisocyanate (NCO) was used as hardener. The identical peak for NCO group has been reported in the FTIR spectra at the peak of 2280 cm^{-1} [15,16] which also can be seen in Fig. 7. When the hardener cures the polyester-epoxy resin, an NH– bond will be formed. Hence there should be no NCO band but NH vibration band should be observed in the FTIR spectrum. From the FTIR analysis, there were no NCO bands observed in the peak range for all binder systems, as seen in Fig. 7. As expected, a new peak appears between 1506-1525 cm^{-1}, indicates the formation of NH- bond which results from the cross-linking between resins and the curing agent. 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 [6]. For all samples analysis, there was very broad peak occur at range of 3370 cm^{-1}, representing the presence of OH functional group which also play role in the adhesion and cross-linking process within samples as it is source of hydrogen bonds for the binder systems [18].

4. CONCLUSIONS

Electrochemical impedance spectroscopy (EIS) study is a valuable test method since it can be detailed data relating to the performance and quality of the coating. EIS study revealed that for the 30 days of exposure to 3.5% NaCl solution, the 90P10E coating system has excellent coating performance due to the contribution of highest coating resistance, R_c, lowest double layer capacitance, C_{dl} as well as lower water uptake, $\emptyset$ and dielectric constant, ε compared to other coating systems. Thus, it can be predicted that the 90P10E coating system can well prevent the steel panel from corrosion production which can be useful for exterior applications. FTIR analysis can determine the functional group and cross-linking occur in the coating samples.

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