

## Evaluation and Prediction of Corrosion Resistance of Epoxy Systems and Epoxy/Polyurethane Systems in Seawater Environment

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Current coating practice requires the thickness of anti-corrosion organic coatings to be over 250  $\mu\text{m}$  for immersion parts of ships and offshore structures and the corrosion resistance of these coatings has been evaluated by destructive and qualitative analysis. Recently, Electrochemical Impedance Spectroscopy(EIS) method has been employed, as an alternative, to evaluate corrosion resistance of organic coatings. This method is characterized as being nondestructive, reproducible, and quantitative in evaluating aging of organic coatings. In this study, EIS method was adopted to quantitatively and effectively select the coating systems having optimized protective performance. Evaluations of several epoxy and epoxy/polyurethane coating systems typically used for ships and offshore structures were carried out in wet(50  $^{\circ}\text{C}$ , 90  $^{\circ}\text{C}$ ) and dry(room temp.) environments to accelerate the degradation of the organic coatings. These results were compared with the conventional scribed(scratched) test results. The plausible prediction model for determining the remaining life-time of coating systems was also proposed based on variations of impedance data, FT-IR and  $T_g$  measurements results.

**Keywords** : organic coating, electrochemical impedance spectroscopy(EIS), epoxy, polyurethane, life-time prediction

### 1. Introduction

Organic coatings have been widely used to protect steels and other metals in corrosive environments due to their good physical, chemical, mechanical performance, and low cost. Many kinds of organic coatings have been also applied to protect ships and offshore structures in various corrosion environments. As the required useful life-time of these structures increases lately, the concerns for corrosion protection of ship/offshore structures have been greatly increased.

Current coating practice requires the thickness of anti-corrosion organic coatings to be over 250  $\mu\text{m}$  for seawater immersion parts of ships and offshore structures and the protective performance of these coatings has been evaluated by destructive and qualitative analysis such as salt fog spray, sea water immersion, weathering, and so on.<sup>1)</sup> These destructive tests have long been used for assessing the corrosion resistance of organic coatings, but there is persistent dissatisfaction regarding the reliability

of correlation between such tests and the actual field performance. In addition to lack of correlation with real environmental situation, destructive tests based on visual monitoring of coating failure, which have relatively poor reliability, require longer test duration as well as unable to predict the remaining useful life-time of the coatings.<sup>1) 2)</sup>

Considering the rather harsh service environments of marine vessels and offshore structures, therefore, it is desirable to develop more quantitative and effective approach to evaluate the organic coating systems in terms of their protective performance and to predict coating's useful life-time. Recently, Electrochemical Impedance Spectroscopy(EIS) method has been applied, as an alternative, to evaluate corrosion resistance of organic coatings, which is characterized as being nondestructive, reproducible, and quantitative in evaluating aging of organic coatings.<sup>3),4)</sup>

In this investigation, EIS method was adopted to select the coating systems with optimized protective performance under seawater environment. The evaluation of several epoxy and epoxy/polyurethane coating systems, typically

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used for ships and offshore structures, was carried out in wet(50 °C, 90 °C) and dry(room temp.) environments to accelerate the degradation of the organic coatings. These results were compared with the conventional scribed (scratched) test results. The plausible prediction model for determining the remaining useful life-time of coating systems was also proposed based on variations of impedance data, FT-IR and T<sub>g</sub> measurements results.

## 2. Experimental methods

### 2.1 Specimen preparation and test conditions

Epoxy and epoxy/polyurethane coating systems were selected for evaluation, which are representative systems for water ballast tank of ship and splash zone of offshore structure, respectively. Brief information and designation for each coating systems are summarized in Table 1. As substrates, carbon steel plates, having dimension of 150 mm×75 mm×2.5 mm(t), were used after acetone cleaning, and blasting to Sa 1 Gr.

All coated coupons were exposed to accelerated corrosion tests under scribed(scratched) or unscribed condition. The scribed(scratched) coupons having a scribe line of 50 mm×1 mm were subjected to destructive test, whereas the unscribed ones were used for EIS measurement. Cyclic test alternating the wet condition at high temperature(50 °C or 90 °C) and dry condition at room temperature was periodically repeated to accelerate the degradation of the applied organic coatings. The procedures and conditions are shown in Table 2.

**Table 1. Selected coating systems for ship and offshore structure**

Applied Section	Coating Systems and Designation	Dry Film Thickness
Ship (water ballast tank)	E1 Tar-free Epoxy A(1st)	100 μm
	E2 Tar-free Epoxy A(1st)	150 μm
	E3 Tar-free Epoxy A(1st) + Tar-free Epoxy A(2nd)	300 μm
Offshore Structure (splash zone)	EU Epoxy Zinc A(1st)	50 μm
	High-build Epoxy B(2nd)	150 μm
	Polyurethane A(3rd)	60 μm

**Table 2. Test conditions and test sequences**

Test Condition	Test Sequences
Wet(50°C) & Dry	Immersion(50°C, NS) & EIS measurement(RT, NS)
	5 days
Wet(90°C) & Dry	Immersion(90°C, NS) & EIS measurement(RT, NS)
	5 days

\*RT: Room Temperature, \*\*NS: Natural Seawater

### 2.2 EIS measurement

EIS measures the AC electrical resistance(impedance) of a coated film at different frequencies and has become a good tool to evaluate the barrier properties of organic coatings.<sup>4)</sup> The impedance was measured with an electrochemical cell having 13.9 cm<sup>2</sup> of exposure area. Two electrode systems were used and carbon electrode was used as a counter electrode. EIS measurements were conducted in natural seawater at room temperature using a frequency response analyzer(Solatron™ 1260/1296A) and dedicated software(ZPlot & Zview™). The scanning frequency was ranged from 100 kHz to 10 mHz with an imposed voltage amplitude of 50 mV(rms).

### 2.3 DSC and FT-IR

Differential Scanning Calorimeter(DSC) and Fourier Transform Infrared Spectroscopy(FT-IR) were used to characterize organic coatings used in this study. DSC analysis yielded the glass transition temperature(T<sub>g</sub>), and FT-IR provided molecular structure related information. For DSC measurement, the specimens(5mg) were carefully peeled from the coated film and DSC scans were carried out from 0 °C to 120 °C at ramp rate of 10 °C/min by using a DSC(PerkinElmer™, PYRIS DIAMOND™). FT-IR analysis was carried out both before and after cyclic corrosion test - wet(90°C/50°C) and dry(RT) - to elucidate the molecular structure change or chemical reaction caused by coating degradation. FT-IR was measured under resolution 8 cm<sup>-1</sup> and 32 scan times using an infrared spectrometer(Thermo Nicolet™).

## 3. Results and discussion

### 3.1 Coating protective performance : destructive evaluation

Evaluation result of protective performance of each coating systems with scribed condition are shown in Fig. 1 and Fig. 2. After 8 cycles, protective performance of each coating systems exposed to cyclic (wet at 50 °C and dry at room temperature) environment was graded as follows;

$$EU > E3 > E2 > E1$$

Blistering was found for E1 and E2 coating systems due to lower dry film thickness. Generally, the thicker coating thickness provides better protective performance in the same coating system, considering the barrier effect of the coating layer against moisture and oxygen permeation. On the other hand, the coating protective performance of EU was relatively superior to that of E3,

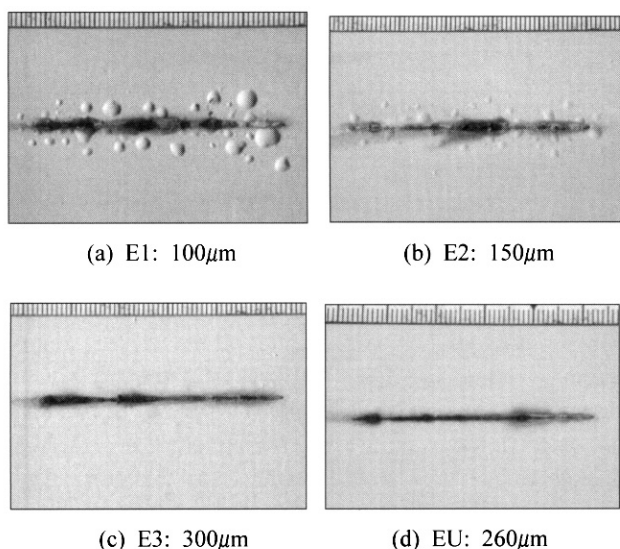


Fig. 1. Test results of scribed specimens in wet(50°C) & dry(room temp.) after 8 cycles

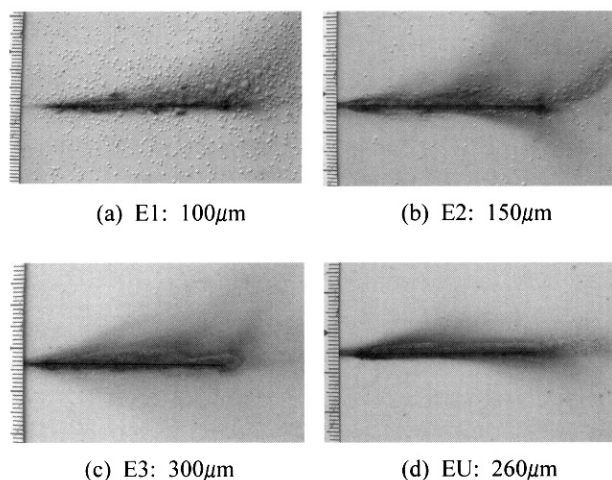


Fig. 2. Test results of scribed specimens in wet(90°C) & dry(room temp.) after 4 cycles

despite the thickness of EU(epoxy/ polyurethane) system was thinner than that of E3(epoxy/epoxy). This difference was attributed to better barrier effect of the polymer systems against corrosive media, such as water, oxygen, and electrolyte.

The coating protective performance in wet(90 °C) and dry(RT) environment after 4 cycles was also as follows;

$$EU > E3 > E2 > E1$$

In this case, the wet test temperature, 90 °C, was seemed to be too high to provide appropriate evaluation and the results failed to provide clear differences for each coating systems as shown in Fig. 2. Under this test condition, all

of the organic coatings were severely degraded regardless of the scribe and resulted in the rapid aging of coating. The cause of this result is summarized the latter part of this paper.

### 3.2 Coating protective performance : EIS evaluation

EIS measurement results were presented in Fig. 3 as in the form of Bode. Initial coating protective performance was proportional to coating thickness as shown in Fig. 3(a). As the increase of exposure time to corrosion environment for each coating system, the inherent protective property of each coating system was revealed. The EIS measurement after 20 cycles in wet at 50 °C and dry at room temperature were shown in Fig. 3(b). The test results showed high reproducibility. Protective performance of each coating to corrosion was graded as follows, and the tendency was the same as the test results from the scribed coupons, described above;

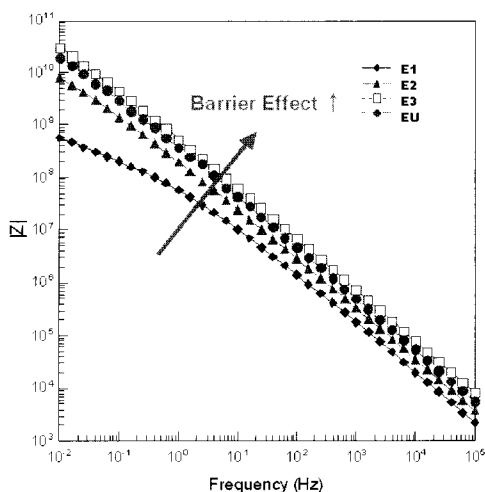
$$EU > E3 > E2 > E1$$

The impedance of an organic coating is related to its permeability to water, and other corrosive media. The higher the impedance of a coating, the lower its permeability to corrosives, hence the more protective coating is anticipated to be as the result. On the other hand, low impedance implies a high permeability and possibly early development of under film corrosion.<sup>5)</sup> The most of test result from this study was quite consistent with these observations. The only notable difference is, as shown in Fig. 3(c), the EIS measurement results in wet 90 °C and dry condition. The result implicated that it was impossible to rank coating protective performance and difficult to attain distinctive and reliable results which were probably considered due to the coating property change caused by very high wet temperature. Therefore, the selection of wet test temperature was very important for adequate evaluation of organic coating in cyclic wet and dry test.

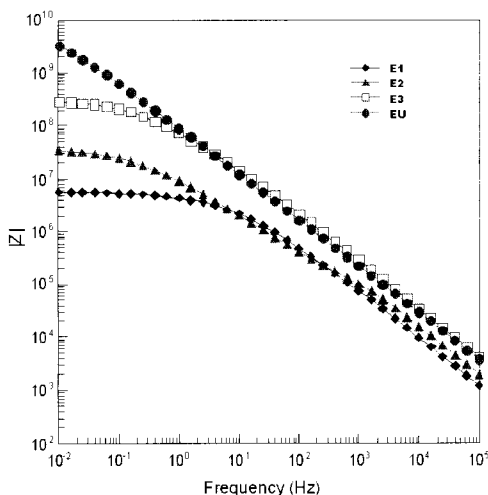
### 3.3 Coating analysis by DSC and FT-IR

DSC analysis was carried out before cyclic wet/dry test to measure the glass transition temperature( $T_g$ ). The attained  $T_g$  values by DSC analysis, as summarized in Table 3, clearly indicates that  $T_g$  values are different for all coating materials. Considering the  $T_g$  values, it is noticeable that one of the test temperature, 90 °C, is far higher the measured  $T_g$ , thus it can be easily assumed that severe degradation of coated film's barrier property would occurred during the cyclic test.

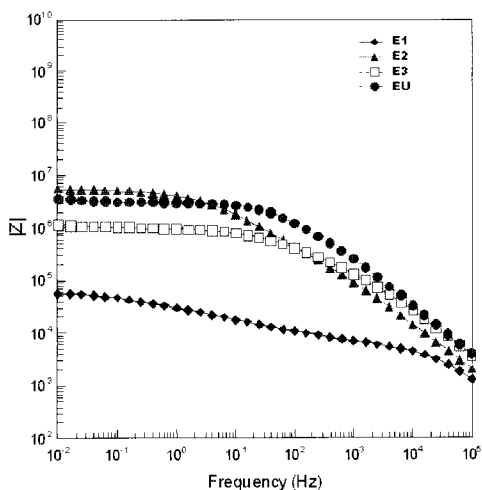
Generally, it is known that the barrier properties experience an abrupt decrease when the exposure tem-



(a) Initial condition



(b) After 20 cycles of wet(50°C) & dry(room temp.) exposure



(c) After 4 cycles of wet(90°C) & dry(room temp.) exposure  
**Fig. 3.** Bode plots organic coatings before/after corrosion tests

**Table 3.** T<sub>g</sub> values for each coatings

Coating Type (Designation)	T <sub>g</sub> (°C)	Remarks
Epoxy A (E1)	60.63	-
Epoxy Zinc A (E2)	50	data obtained from paint maker
Epoxy B (E3)	70	
Polyurethane A (E4)	43	

perature was higher than the T<sub>g</sub> of the coating during thermal cycling EIS test,<sup>6)</sup> and by the same token some researchers proposed that the exposure temperature should not exceed the coating's T<sub>g</sub> during the test otherwise unexpected failures would result.<sup>7)</sup> On the other hand, when wet setting temperature is 50 °C, which is slightly higher or lower than coated films' T<sub>g</sub>, the results was reasonable. Since the selection of much higher than T<sub>g</sub> to accelerate coating degradation often cause improper and unpredictable results. Therefore, it seems to be critical that to select wet test temperature carefully to attain reliable test results.

FI-IR analysis was conducted before and after cyclic wet/dry test to confirm the chemical molecular structure change caused by coating degradation. Fig. 4(a) and (b) showed FT-IR analysis results for E3(Epoxy/Epoxy, 300 μm) and EU(Epoxy/Polyurethane, 260 μm) after 8 cyclic aging in wet(at 90°C) & dry(at room temp.) condition along with initial coating condition. Observation of epoxy functional group( $\begin{matrix} \diagup & \diagdown \\ & \text{C} \\ \diagdown & \diagup \\ & \text{O} \end{matrix}$ ) at 915 cm<sup>-1</sup> peak in Fig. 4(a) showed that the resin was typical epoxy type. After 8 cycles, the absorption peak of Aromatic alkene(CH<sub>2</sub>, 2920 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>) and phenyl( $\text{C}_6\text{H}_5$ , 1380 cm<sup>-1</sup>, 1225 cm<sup>-1</sup>) in which epoxy resin peak was remarkably dropped and nearly indistinguishable. This means that the molecular bond of epoxy resin was partially broken into monomers, which were dissolved into electrolyte during coating aging.

In Fig. 4(b), absorption peaks(1660 cm<sup>-1</sup>, 1350–1460 cm<sup>-1</sup>) of the functional group of urethane ( $\begin{matrix} \text{O} & \text{H} \\ \parallel & | \\ -\text{C} & -\text{N}- \end{matrix}$ ) and ester( $\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{matrix}$ ), respectively, were also considerably decreased and became indistinguishable. The talc pigment contained in epoxy(second coating) was also detected, indicating that the partial molecule of polyurethane was compromised and dissolved, thus changing it's molecular structure.

Fig. 5(a) and (b) showed FT-IR analysis results of E1 and EU coating system before and after wet(at 50 °C)/dry(at room temperature) test. Degradation of organic coating was occurred, whereas the chemical molecular

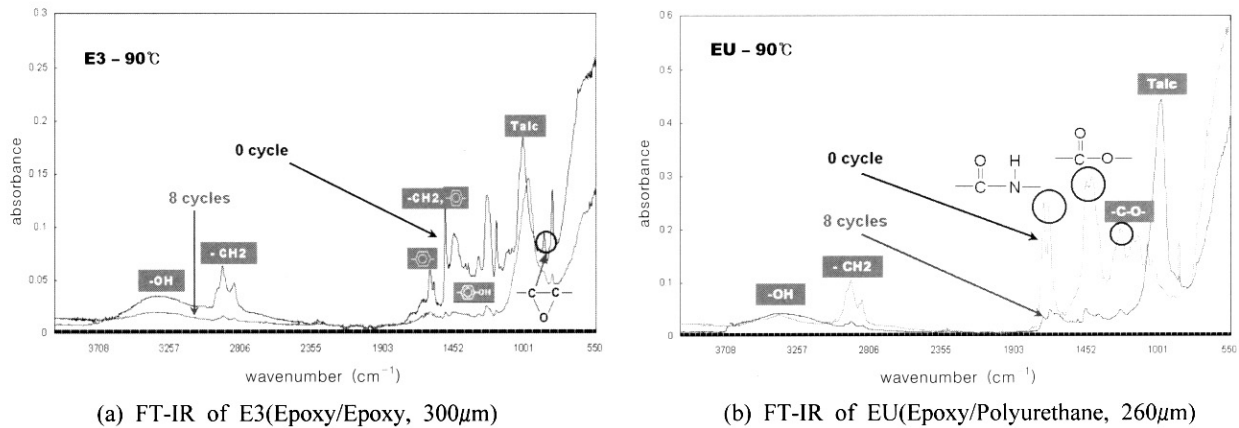


Fig. 4. FT-IR results for E3 and EU before/after wet(90°C) and dry test

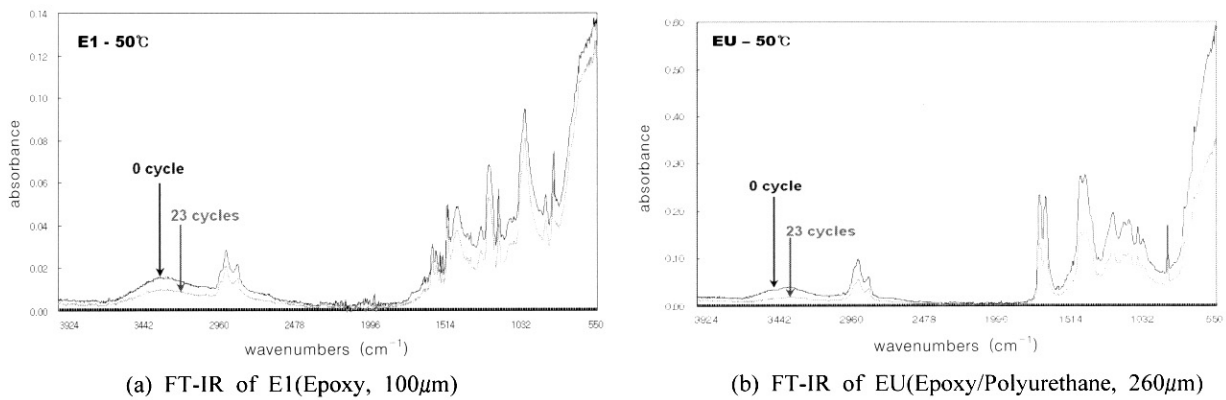


Fig. 5. FT-IR results for E1 and EU before/after wet(50°C) and dry test

structure was not changed. Therefore, temperature of 50 °C for the coating systems was verified to be proper test regime. These results strongly supports that it is necessary to examine  $T_g$  of coating material before initiation of accelerated test at high temperature, whereas the optimal temperature regime for acceleration of coating's aging is yet to be clarified.

### 3.4 Prediction of coating life time

An organic coating system's electrical resistance or impedance is a general indicator of its anti-corrosion performance. For example, an organic coating with initial resistance higher than  $10^8 \Omega\text{cm}^{-2}$  typically provides excellent corrosion protection whereas those having lower resistance of approximately  $10^6 \Omega\text{cm}^{-2} \sim 10^7 \Omega\text{cm}^{-2}$  provide poor corrosion protection.<sup>4),8)</sup>

To predict the remaining life-time of coatings by EIS measurement, the impedance(Z) of coatings in wet(50 °C) and dry conditions were measured at frequency 0.1Hz in bode plot with exposure time(t) and plotted in Fig. 6. As the exposure time increased in Fig. 6, the impedance

values decreased and the absolute value was high as the order of EU, E3, E2, and E1. Impedance and related coating performance of EU, despite of lower thickness, was much higher than E3 and maintained above  $10^8 \Omega\text{cm}^{-2}$  after 23 cycles. These results suggests that this plot can to be used as a comparison tool for several coating systems in terms of their anti-corrosion performance between coatings as well as for determining the maintenance

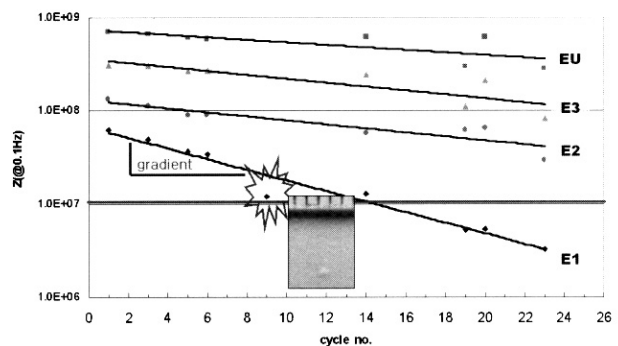


Fig. 6. Impedance vs. time with various environments

**Table 4. Ageing rate and reliability of coating systems with test methods**

Coating Systems		Gradient (Aging rate)	Reliability
Epoxy	E1	- 0.13	0.96
	E2	- 0.05	0.82
	E3	- 0.048	0.72
Epoxy / Polyurethane	EU	- 0.03	0.53

window as a function of exposure duration during actual service.

It was found that blistering occurred when impedance Log Z was downed to near about 7. Once blistering occurred, the coating's corrosion resistance is expected to decrease heavily and repair of the existing coating should be considered. Therefore, it is possible to predict the blistering initiation duration of each coating by reading the time when the trend line reaches the impedance about  $10^7 \Omega\text{cm}^{-2}$  via x-axis extrapolation. Table 4 summarized gradient values for each coatings obtained from the trend line in Fig. 6. It indicated that the gradient regarded as the degradation rate and its reliability for prediction of coating life-time in wet and dry environment can be assessed, as shown the Table 4. The reliability was fairly good and the degradation rate of coatings and reliability were inversely proportional to coating thickness in the identical coating systems. But, it is required that coatings over  $260 \mu\text{m}$  thickness need additional measurement for higher accuracy in life-time prediction. In addition, it is further studied how many fractions apply for real environment.

#### 4. Conclusions

1. Corrosion resistances of coatings evaluated by EIS

(unscribed) measurements and conventional scribed(or scratched) tests were as follow;  
Epoxy/Urethane( $260 \mu\text{m}$ ) > Epoxy/Epoxy( $300 \mu\text{m}$ ) > Epoxy( $150 \mu\text{m}$ ) > Epoxy( $100 \mu\text{m}$ )

2. Selecting test temperature higher than Tg to accelerate coating degradation would cause improper and unpredictable results. It is necessary, thus, to select test temperature for wet cycle to attain reliable results. Especially, when the wet test temperature was around  $90^\circ\text{C}$ , the molecular bond of epoxy resin was partially broken into monomers, dissolved into electrolyte during coating aging.

3. By quantitatively assessing aging process of organic coatings with exposure duration using EIS, it is possible to predict useful life-time of organic coating by reading the extrapolated time at  $10^7 \Omega\text{cm}^{-2}$  impedance from the blistering initiation observation time.

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