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Evaluation of Corrosion Protection for Epoxy and Urethane Coating by EIS under Various Cyclic Corrosion Tests

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Protective coatings play an important role in the protection of metallic structures against corrosive environment. The main function of anticorrosive coating is to prevent the materials from corrosive agents, such as water, oxygen and ions. In the study, the corrosion protection properties of urethane and epoxy coating systems were evaluated using EIS methods exposed to the corrosion acceleration test such as Norsok M501, Prohesion and hygrothermal cyclic test. AFM analysis of the coating systems was carried out to monitor the change of roughness of coatings. Urethane coating system was more stable than the epoxy coating under given cyclic conditions. Water uptake into the urethane coatings was less than that into the epoxy coating. The urethane coating system showed better corrosion protection than epoxy coating system based on the changes of the impedance modulus at low frequency region with exposure time. Consequently, the corrosion protection properties of the epoxy and urethane coatings was well correspond with their surface roughness changes and water uptakes.

Keywords *: EIS, AFM, NORSOK, organic coating*

1. Introduction

Reliable evaluation methods of organic coatings for corrosion protection are required by coating industries. For this purpose, various test methods have been developed and applied for many years. Outdoor exposure tests are considered as reliable test method and it can provide a good indication of the actual service life of coating. However, outdoor exposure tests generally require very long test time. On the other hand, an accelerate test very often disagrees with the actual degradation mechanisms which occurred under natural conditions. In fact, in order to design an acceleration condition, it is necessary to increase the levels of natural parameters affecting the corrosion protection properties of a coating. In general, acceleration factors can be obtained by controlling the concentration of corrosive material, such as the change of pH and temperature, etc.

Many evaluation tests and techniques for coatings have been examined and applied in recent years to reduce the test time and improve their reliability. The most commonly used method is salt-spray testing following the ISO 7253 standard[1)] which was introduced by modifying chemical composition of the test solution, or by introducing several degradation steps in one cycle. Skerry and Simpson[2)] proposed the Prohesion test (ASTM G85) with an alternate cycle of UV and continuous condensation. Chong et al[3)] created a modification of the ASTM D 5894 cycle and added low temperature step. The Norsok M 501 test is a standardized Norwegian weathering test which designed for very severe offshore structure. In this cyclic test, the described coated panel undergoes sessions of UV exposure with humidity, salt fog and a conditioning period at room temperature as the dry part of the cycle. Bierwagen et al. studied[4)-5)] the electrochemical behavior of organic coats. The temperature of the sample is controlled above and below the glass transition temperature to establish a synergic degradation effect into the material. This cyclic process can induce the electrolyte penetration into the coating and result in electrolyte accumulation, loss of adhesion, chemical and physical ageing as a consequence of thermal fatigue effects. These cumulative effects can give the reasonable results just in a week. In addition to the cyclic process, EIS test methods are also applied in the evaluation of coatings in various corrosive environments.[6)-10)]

The research objective of the present work is to examine

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the corrosion protection of epoxy and urethane coating by various suggested cyclic test, including Norsok M501, prohesion and hygrothermal cyclic test and these will be analyzed by AFM, water penetration behavior and EIS.

2. Experimental

2.1 Specimen preparation of epoxy coated carbon steel

Diglycidyl ether bisphenol-A (DGEBA) based epoxy coating and Toluene diisocyanate (TDI) based urethane coating were used to prepare the coating film. Carbon steel sheet (15 mm × 70mm × 2.5 mm thick) was pretreated by blasting of steel grit as Sa 2.5, degreased by ethyl alcohol in ultrasonic bath for 10min, and then dried in a convection oven. The average surface roughness of carbon steel was measured to be about 40~65 ㎛. The epoxy and urethane coating were sprayed on the surface of the carbon steel to 125 ㎛ thick by the air spray method. The coated specimens were then cured in an oven for 2 weeks at 25 ℃.

2.2 NORSOK M 501 cyclic test

NORSOK M 501 cyclic tests were conducted to accelerate the cumulative effects of electrolyte on the coating/metal interface through the diffusion of electrolyte into the coating. Each cycle is consisted of 72 h of Q-UV with condensation, 72 h of salt spray and 16 h of air drying. Total 16 cycles of test were carried out and test equipment was shown in Fig. 1.

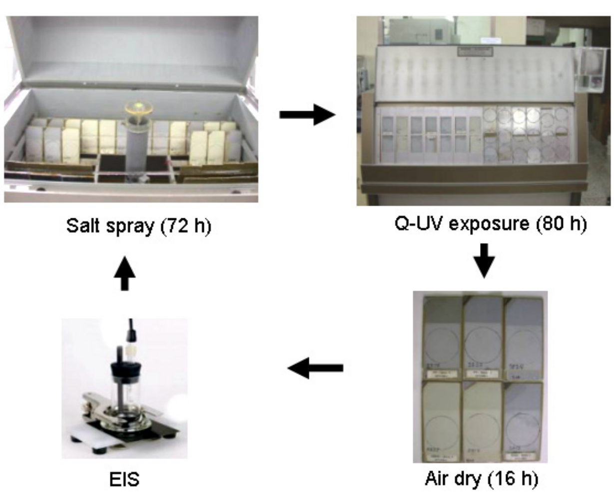

Fig. 1. The test procedure of Norsok M 501 cyclic test.

2.3 Prohesion test

Prohesion test method is less severe than standard salt spray tests and generally regarded as giving a better correlation with outdoor exposure results. An aqueous solution containing 0.05% sodium chloride and 0.35 % ammonium sulphate is used for prohesion test. The test cycle consists of 1 hour exposure to salt mist at ambient temperature followed by 1 hour drying at 35 °C. Total 16 weeks of test were carried out and test equipment is shown in Fig. 2.

Fig. 2. Prohesion test equipment.

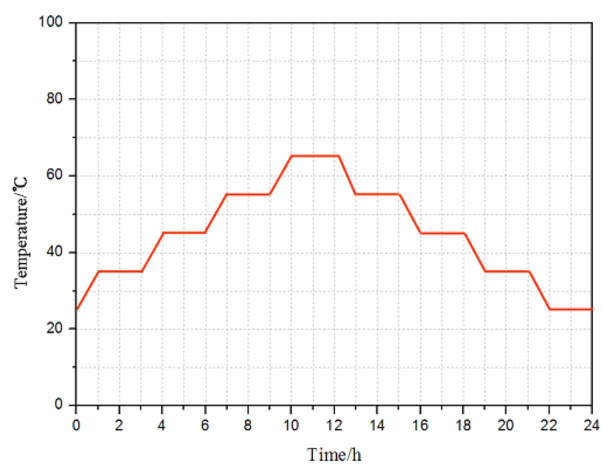

Fig. 3. Heating and cooling cycles used in the hygrothermal cyclic test.

2.4 Hygrothermal cyclic test

Hygrothermal cyclic tests were conducted to accelerate the cumulative effects of electrolyte on the coating/metal interface through the diffusion of electrolyte into the coating. The thermal cycle employed in the test was shown in Fig. 3.

2.5 Surface topology analysis of coatings by AFM

The surface topography of cured epoxy and urethane coatings was studied by Atomic Force Microscopy (Seiko, AFM). The scanned area was 80 × 80 ㎛ and frequency was 0.3 Hz. Surface topology of epoxy and urethane coatings including the surface roughness was examined follwing the Norsok M 501, prohesion and hygrothermal cyclic tests.

2.6 Electrochemical impedance spectroscopy combined with cyclic tests

EIS was performed at the open circuit potential, using an EG&G 273A potentiostat, Solatron1260 FRA. Three electrode electrochemical cell consisted of the coated carbon steel as a working electrode (exposed area: 13.9 cm^2), a saturated calomel reference electrode, and a carbon counter electrode was used to conduct electrochemical impedance spectroscopy (EIS) test at corrosion potential in 0.5 N NaCl solution. The impedance modulus of epoxy and urethane coated carbon steels were calculated by Z-view software. In present study, data were obtained by applying a sine wave of 50 mV amplitude as a function of frequency ranged from 100 kHz to 10 mHz.

To investigate the diffusion of water through the modified epoxy coatings, the volume fraction of water uptake and the diffusion coefficient of water through the coating were calculated by measuring the capacitance of the coating. Brasher and Kinsbury[11)-14)] suggested an empirical expression that relates the capacitance of a coating to the volume fraction of water absorbed into the coating, which was expressed by

$$V_t = \frac{100 \log(C_t/C_0)}{\log \varepsilon_{H_2O}} \qquad (1)$$

where V_t is volume fraction of absorbed water at time t, C_0 and C_t are the capacitances of an organic coating at time t = 0 and at time = t, respectively, and ε_{H2O} is the dielectric constant of water (80 at T = 20 °C)

3. Results and discussion

3.1 Surface topology of coatings with respect to cyclic tests

To examine the coating surface on a microscopic level by cyclic test including Norsok M 501, prohesion and hygrothermal cyclic tests, the surface roughness and surface topography of the epoxy and urethane coated specimens were examined by AFM.

Fig. 4 shows the AFM images of epoxy coating system in terms of Norsok M 501, prohesion and hygrothermal cycles, respectively. In case of prohesion and hygrothermal cycles, the surface roughness of epoxy coating system showed similar changes to 5.42 and 5.88 μm with respect to cycles. However, the surface roughness of epoxy coating system has become much higher to 6.86 μm by Norsok M 501 cyclic test. The main cause of roughness changes for epoxy coating system by prohesion and hygrothermal cycles may be caused by absorption and desorption of water through the cycles. The increasing of roughness changes for epoxy coating system by Norsok M 501 cyclic test seems to be the ageing of epoxy coating by the exposure of ultraviolet.

Fig. 5 shows the AFM images of urethane coating system in terms of Norsok M 501, prohesion and hygrothermal cycles, respectively. The roughness changes for urethane coating system were less than those of epoxy coating system but the trend of surface roughness changes was very similar to the epoxy coating system. In prohesion

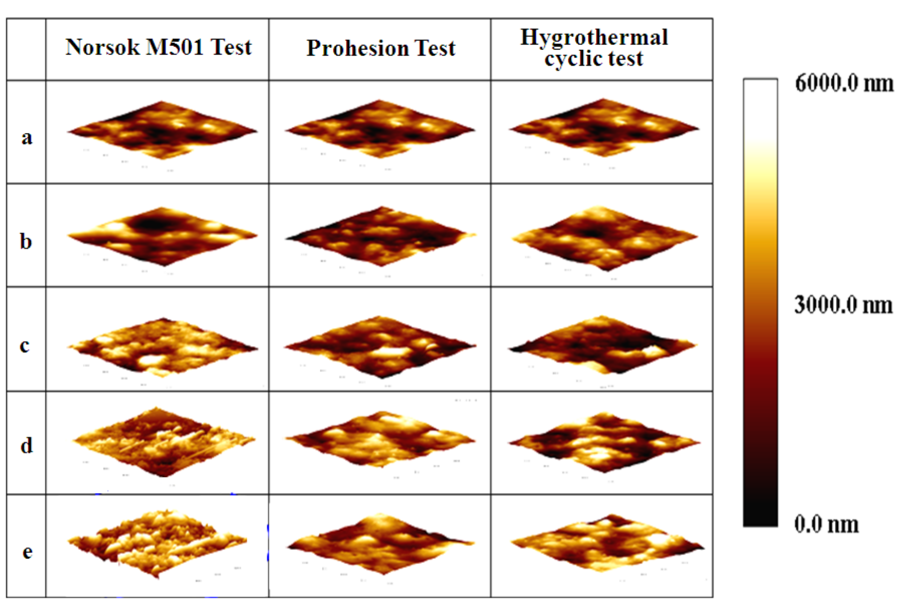

Fig. 4. AFM image of epoxy coating system with cyclic tests; (a) initial, (b) After 4 week, (c) After 8 week (d) After 12 week and (e) After 16 week.

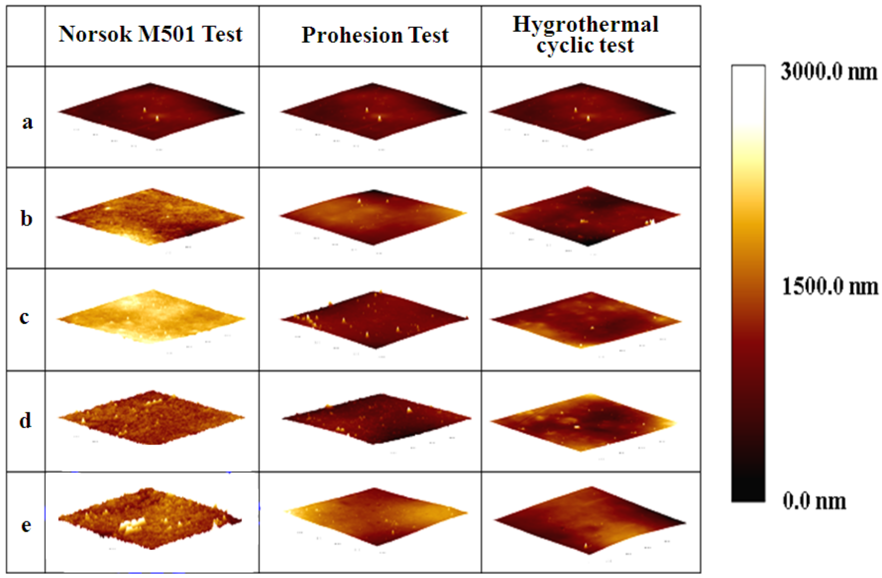

Fig. 5. AFM image of urethane coating system with cyclic tests; (a) initial, (b) After 4 week, (c) After 8 week (d) After 12 week and (e) After 16 week.

and hygrothermal cycles, the surface roughness of urethane coating system showed similar changes to 1.07 and 0.84 μm with respect to cycles. On the other hands, the surface roughness of urethane coating system has become much higher to 3.12 μm by Norsok M 501 cyclic test. The expected mechanism of roughness changes by prohesion and hygrothermal cycles was absorption and desorption of water by cycles. The increasing of roughness changes for urethane coating system by Norsok M 501 cyclic test seems to be the ageing of urethane coating by the exposure of ultraviolet.

From the results of AFM examination, it was noticed that the urethane coating system was more stable than the epoxy coating with Norsok M 501, prohesion and hygrothermal cyclic conditions.

3.2 Water uptakes and corrosion protection measured by EIS analysis

As previous study, water uptakes of coatings were calculated using capacitance of a coating at the frequency of 10 kHz. Fig. 6 shows water uptakes of epoxy coating depending on the cycles of Norsok M 501, prohesion and hygrothermal cycles, respectively. The water uptake in the coating increased from 3.8 vol.% to 7.0 vol.% at 25 °C with an increase in cycles when the specimens were exposed to prohesion and hygrothermal cyclic tests. On the other hands, the water uptake of epoxy coating has been increased much higher to 12.5 vol% by Norsok M 501 cyclic test.

Fig. 7 shows water uptakes of urethane coating depend-

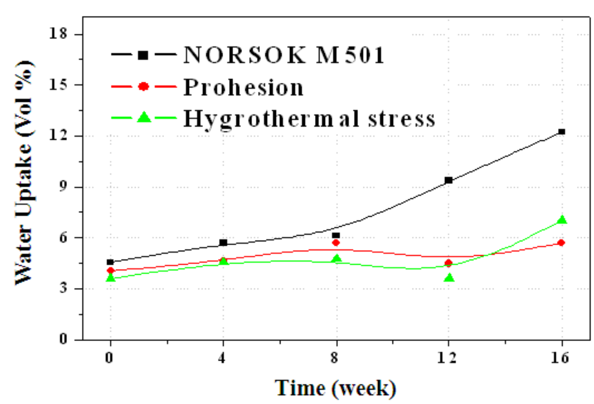

Fig. 6. Water uptakes curve for epoxy coatings by diverse cyclic tests.

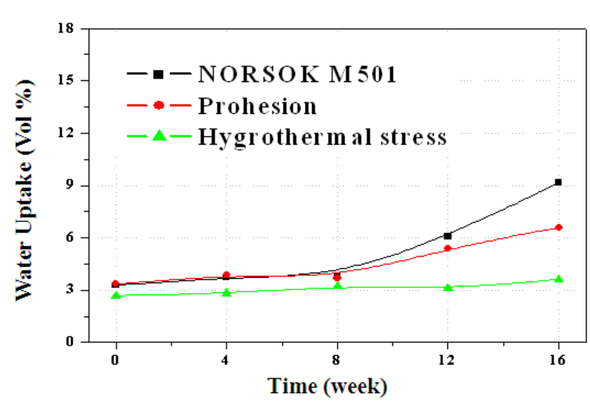

Fig. 7. Water uptakes curve for urethane coatings by diverse cyclic tests.

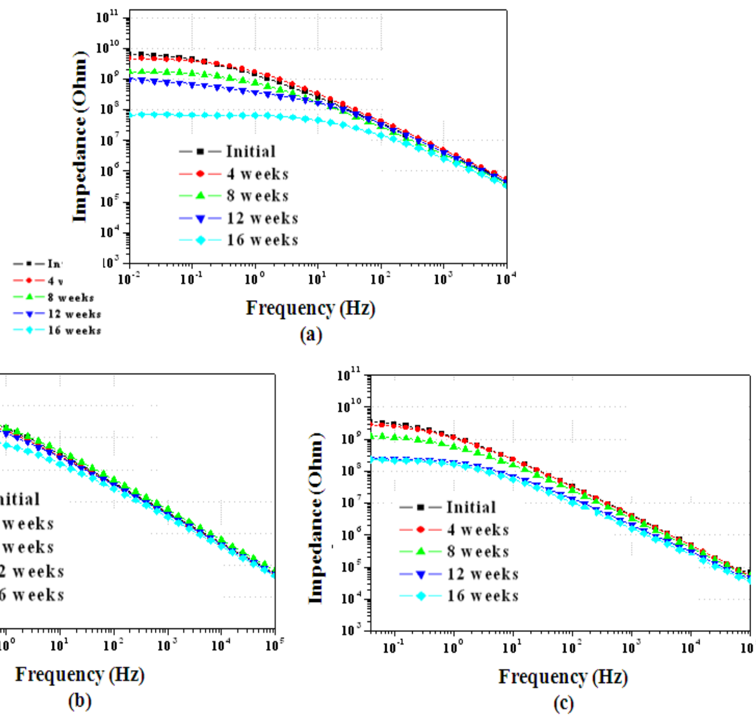

Fig. 8. EIS spectra in Bode plot for epoxy coating as a function of exposed time: (a) Norsok M 501, (b) prohesion test and (c) hygrothermal cyclic test.

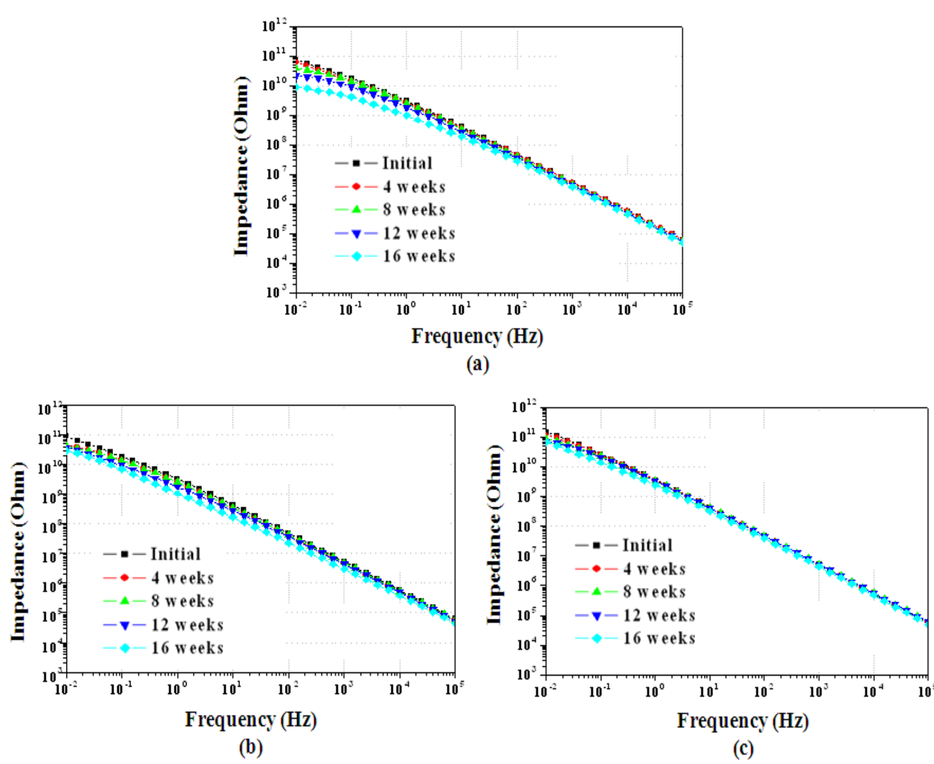

Fig. 9. EIS spectra in Bode plot for urethane coating as a function of exposed time: (a) Norsok M 501, and, (b) prohesion test and (c) hygrothermal cyclic test.

ing on the cycles of Norsok M 501, prohesion and hygrothermal cycles, respectively. The water uptake in the coating increased from 3.0 vol.% to 6.8 vol.% at 25 °C with an increase in number of cycles when the specimens were exposed to prohesion and hygrothermal cyclic tests. On the other hands, the water uptake of epoxy coating has been increased much higher to 9.1 vol% by Norsok M 501 cyclic test.

These results clearly demonstrate that diffusion rate of water in the epoxy coatings is faster than that of the urethane coating, hence the water uptake into the epoxy coatings is higher than that into the urethane coating. The effect of cyclic test on the water uptakes is more appreciable with Norsok M 501 for a given coating systems.

The corrosion protection of the epoxy and urethane coated steels was examined by EIS combined with Norsok M 501, prohesion and hygrothermal cyclic conditions.

Fig. 8 shows the EIS results of epoxy coated steel. The impedance modulus log|Z| at 10^{-2} Hz was measured at 25 ℃, as a function of cycles. In prohesion and hygrothermal cyclic conditions, the impedance modulus decreased from approximately 10^{10} Ω to $5\times10^{8} \sim 10^{9}$ Ω. On the other hands, the log|Z| at 10^{-2} Hz decreased to 9×10^{7} Ω when the specimens were exposed to compared to Norsok M 501 cyclic condition. It is clearly confirmed that the corrosion protection of epoxy coating was decreased much more in Norsok cyclic test than the other cyclic tests.

Fig. 9 shows the EIS results of urethane coated steel. The behavior of impedance of urethane coating is very similar to epoxy coating but decreasing rate of impedance was lower than that of epoxy. In prohesion and hygrothermal cyclic conditions, the impedance modulus decreased from approximately 10^{11} Ω to 5×10^{10} Ω. On the other hands, the impedance modulus decreased to 10^{10} Ω when the specimens were exposed to Norsok M 501 cyclic condition.

Therefore, it is clearly indicated that urethane coating system showed better corrosion protection than epoxy coating system for a given cyclic condition and it was well agreed with the results of water uptakes and surface topology.

4. Conclusions

Conclusions drawn from the work are as follows;

1) The surface roughness of epoxy coating system increased by water uptake under acceleration test used in this study while that of urethane system remained with particular changes

2) Water uptake into the urethane coatings was lower than that into the epoxy coating. The effects of cyclic test on water absorption are more appreciable in Norsok M 501 than the other testing methods

3) The urethane coating system showed better corrosion protection than epoxy coating system suggested by the less decrease in the impedance modulus at low frequency region. Consequently, the corrosion protectiveness of the epoxy and urethane coatings was well agreed with their surface roughness changes and water uptakes.

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