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Study on Hygrothermal Degradation and Corrosion Protection of Epoxy Coatings Cured by Different Amine Based Curing Agents

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Epoxy coatings cured by different amine based curing agents have been prepared. Atomic force microscopy (AFM) has been used to monitor the surface topology changes of epoxy coatings before and after hygrothermal cyclic test. The glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of the epoxy coating were measured by Thermo-mechanical Analysis (TMA). The Electrochemical impedance spectroscopy (EIS) with hygrothermal cyclic test has been introduced to evaluate the corrosion protection of the epoxy coatings. In conclusion, thermal properties of epoxy coatings were in good agreement with the results of corrosion protection of epoxy coated carbon steel obtained result by EIS with hygrothermal cyclic test. The relationship between thermal properties, surface roughness changes and corrosion protection of epoxy coatings are discussed in this study.

Keywords *: Epoxy coating, Hygrothermal, EIS, TMA, AFM*

1. Introduction

Rapid and good reliable evaluation methods of corrosion protection of organic coatings are highly required by coating manufacturer and users. For this purpose, various test methods have been developed and applied for many years. Outdoor exposure tests are considered as high reliable test method and it can provide a good indication of the actual service life of coating. However, outdoor exposure test generally requires long test time and high test cost. On the other hand, an accelerating test is not well matched with corrosion behavior of test samples compared to the results of natural conditions. In fact, in order to determine an acceleration factors, it is necessary to increase the effect of natural parameters affecting the corrosion protection properties of a coating. In general, acceleration effects can be obtained by control of corrosion environments, such as the concentration of electrolyte, the change of pH and temperature, etc.

In order to reduce the testing time and to improve the reliability of test result, various tests and techniques have been studied and performed. The oldest and the most widely used corrosion test method is salt-spray testing (ISO 7253).[1)] Skerry and Simpson[2)] proposed the Prohesion test (ASTM G85) with an alternate cycle of UV and continuous condensation. Chong et al[3)] introduced a modification of the ASTM D 5894 with low temperature step. The Norsok M 501 test is a standardized Norwegian weathering test designed for very harsh offshore environment. In Norsok M 501 test, the described coated panel undergoes cyclic conditions including UV exposure with humidity, salt fog and a room temperature with dry condition. However, these tests usually need several thousand hours to be completed and the evaluation of test results rely on the operators' subjective judgment. Bierwagen et al. reported[4)-5)] the electrochemical behavior of organic coatings. The coated sample was exposed under cyclic test conditions, above and below the glass transition temperature (T_g), to give a synergic degradation effects to the coating layer. The cyclic process accelerates the accumulation of electrolyte into the coating and induces the loss of adhesion, chemical and physical ageing. In addition to the cyclic process, EIS (Electrochemical Impedance Spectroscopy) test method was used to evaluate corrosion resistance of coating in various corrosive environments.[6)-8)]

The aim of this study is to examine the hygrothermal degradation of Diglycidyl ether bisphenol-A (DGEBA)

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based epoxy coating cured by different amine based curing agents.

2. Experimental

2.1 Specimen preparation of epoxy coated carbon steel

Diglycidyl ether bisphenol-A (DGEBA) was used as an epoxy resin. Polyamide (PA) and aromatic diamine (Meta-Xylene Diamine, MXDA) were used as curing agents. Toluene was used as a solvent of the coatings. The molecular structures of epoxy resin and curing agents were shown in Fig. 1.

Epoxy coatings were prepared by mixing DGEBA, PA and MXDA. The mixture was vigorously stirred and degassed for 10 min. The epoxy coatings were applied on Teflon plate using doctor knife and then cured at 25 ℃ for 4 days, followed by post-curing for at 80 ℃ for 4 h to achieve full cure. After the curing, the films were removed for TMA analysis.

Carbon steel sheet (15 mm × 15mm × 3 mm thick) connected with copper wire was embedded in epoxy mold, cured, and used as a working electrode. Surface of the working electrode was pretreated by blasting of aluminum oxide grit, degreased by ethyl alcohol in ultrasonic bath for 10 min, and then dried in a convection oven. The average surface roughness of carbon steel was measured to be about 1 μm. The epoxy coatings were sprayed on the surface of the carbon steel to 100 ± 10 μm thick by the air spray method. The coated specimens were then cured at 25 ℃ for 4 days, followed by post-curing for at 80 ℃ for 4 hours to achieve full cure.

2.2 Thermal performance of epoxy coating with respect to curing agents

Thermo mechanical analyzer (TMA) can measure the T_g of polymer in terms of the change of coefficient of thermal expansion (CTE) because the polymer goes from glass to rubber state with the associated change in free molecular volume. In this study, the T_g and CTE below and above of T_g were measured by TMA (2940, TA Instruments).

The prepared epoxy films were cut with 70 ± 10 μm of thickness, 4 mm of width and 12 mm of length. The cut film were aligned and mounted in film clamp. Then, film clamp was mounted into the film/fiber stage as shown in Fig. 2. . The tests were carried out in accordance with ASTM E 1824-02. The applied force to specimen was 0.05 N and specimens were heated from 10 ℃ to 100 ℃ with

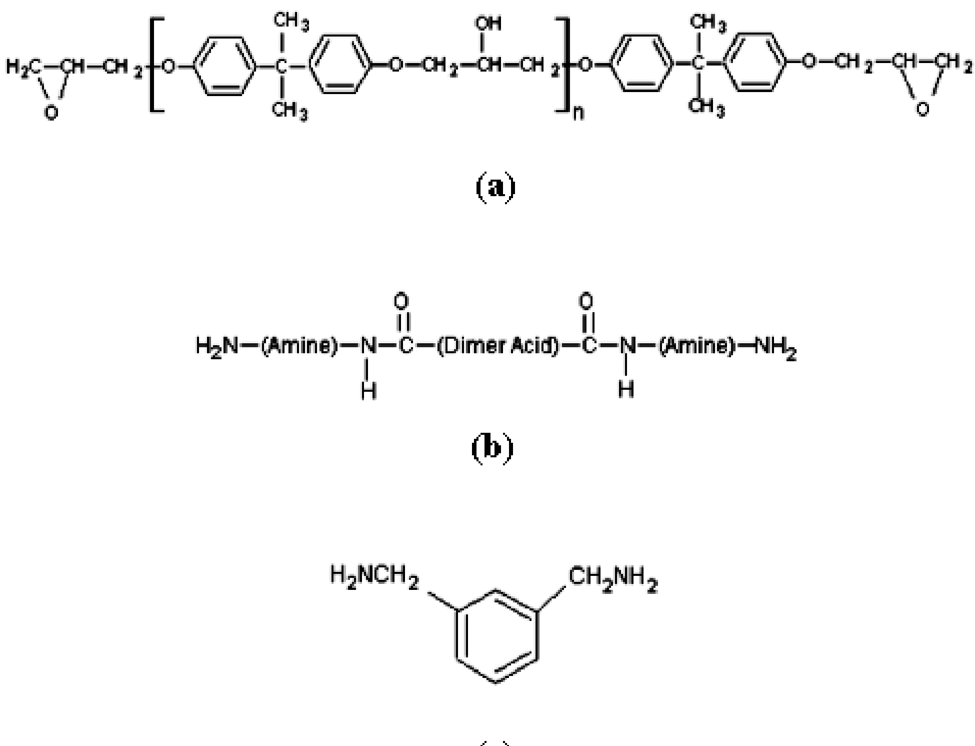


Fig. 1. The molecular structures of epoxy resin and curing agents; (a) Diglycidyl ether bisphenol-A (DGEBA), (b) Polyamide (PA) and (c) Meta-Xylene Diamine (MXDA).

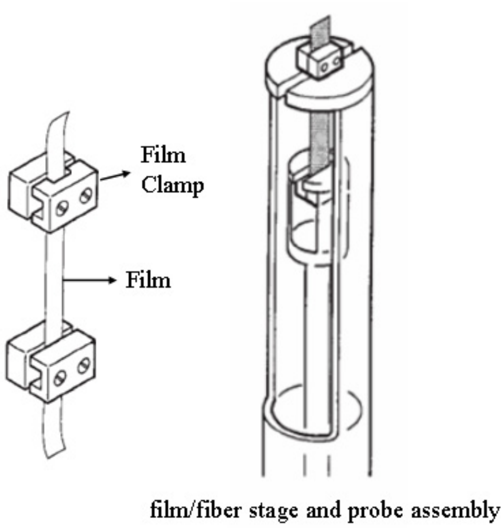


Fig. 2. The film/fiber stage and probe assembly for TMA analysis.

heating rate of 5 ℃/min in N^2 gas.

2.3 Surface topology analysis of epoxy coating by AFM

The surface topography of epoxy coatings was monitored by Atomic Force Microscopy (AFM, Seiko). The epoxy coatings mixed with different curing agents were sprayed on carbon steel and cured. The coating method and curing conditions were same as the specimens for EIS test. The scanned area was 80 × 80 μm using 0.3 Hz. The surface roughness was measured in accordance with hygrothermal cyclic test.

2.4 Electrochemical impedance spectroscopy combined with hygrothermal cyclic test

The impedance modulus of epoxy coating, |Z|, which is measured by EIS is the electrical resistance of the coating. EIS analysis is the most useful method to evaluate the corrosion protection of coating, especially in water immersion or in high humidity environment. The coatings with excellent barrier properties show high impedance modulus, on the other hand, the coatings with low barrier properties show low impedance modulus. In general, when a coating is exposed to an aggressive aqueous environment, its impedance modulus becomes decreases as a function of time. The reason of impedance modulus decrease is reported by an increase of water accumulation into coating and chemical and physical aging.[9)-10)]

Hygrothermal cyclic test is one of the most effective accelerating methods because the increase of temperature of electrolyte can degrade the barrier property of a coating by increase the diffusion rate of electrolyte into the coating layer. As observed in earlier work, if the temperature of electrolyte increases above the T_g, the barrier properties of coating was rapidly decreased.[11)]

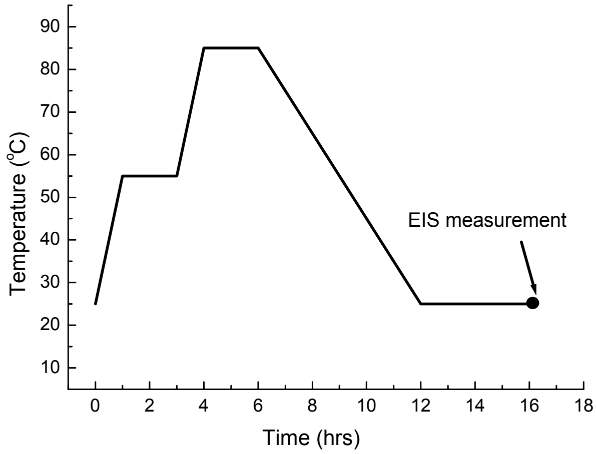


Fig. 3. Hygrothermal cycles for epoxy coated carbon steel.

In this study, hygrothermal cyclic tests were conducted to accelerate the cumulative effects of electrolyte at the coating/metal interface. The applied thermal cycle was shown in Fig. 3. Three electrode electrochemical cell consisted by epoxy coated carbon steel as a working electrode (Exposed area: 225 mm^2), a saturated calomel reference electrode, and a platinum counter electrode was used to conduct EIS test. The working electrode (epoxy coated carbon steel) was immersed in 5 wt.% NaCl solution and the impedance modulus of the epoxy coated carbon steel was measured at 25, 55 and 85 ℃ respectively, in accordance with the hygrothermal cycles.

In order to evaluate the corrosion protection of epoxy coated carbon steel, reversibility (R) was calculated as following calculation

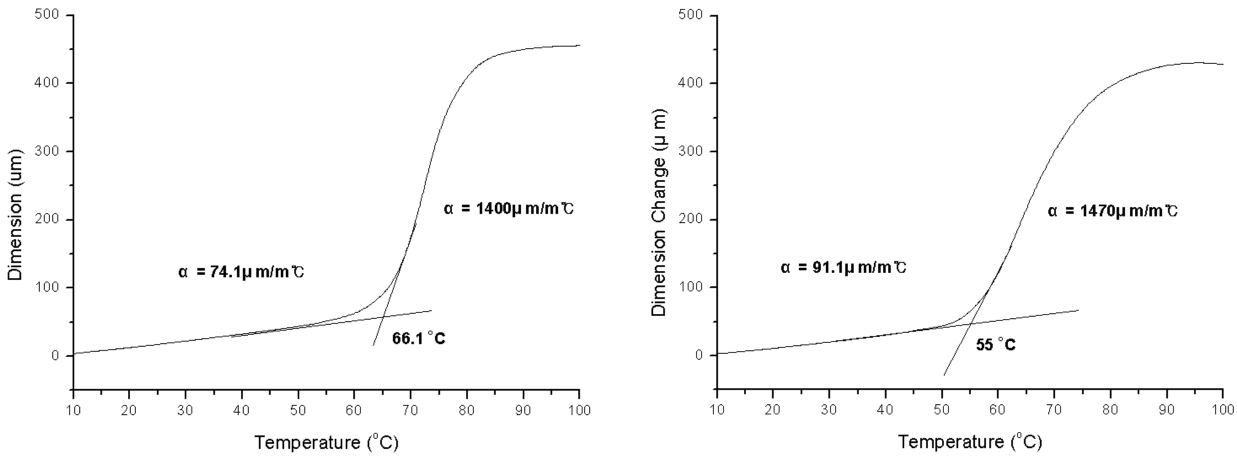
$$R = |Z|_{0.1\text{Hz after thermal cycle}} / |Z|_{0.1\text{Hz at initial}} \quad (1)$$

If the R value is closed to one after hygrothermal cyclic test, it could be inferred that the corrosion protection of coating is not affected by hygrothermal cyclic test. On the other hand, if the R value would show less than one, it could be inferred that the corrosion protection of coating is decreased by hygrothermal cyclic test. The data were obtained by applying a sine wave of 100 mV amplitude as a function of frequency ranged from 100 kHz to 100 mHz.

3. Results and discussion

3.1 Thermal performance of epoxy coating with respect to curing agent

TMA thermograms of DGEBA/PA and DGEBA/MXDA



(a) (b)

Fig. 4. TMA thermograms of epoxy coatings; (a) DGEBA/PA and (b) DGEBA/MXDA.

epoxy coating are shown in Fig. 4. All epoxy coatings exhibit single T_g. The measured T_g (66.1 ℃) of DGEBA/PA epoxy coating was higher than the T_g (55 ℃) of DGEBA/MXDA epoxy coating. The measured CTE of DGEBA/PA epoxy coating below its T_g was 74.1 μm/m℃ and it was lower than that of DGEBA/MXDA epoxy coating (91 μm/m℃).

In case of above T_g, the CTE of DGEBA/PA epoxy coating was dramatically increased compared with the CTE of below T_g. The measured CTE was 1400 μm/m℃ and it was also lower than the CTE of DGEBA/MXDA epoxy coating (1470 μm/m℃) in same condition.

These results clearly indicate that the thermal stability of DGEBA/PA epoxy coating was better than that of DGEBA/MXDA epoxy coating, considering its high T_g and low CTE both below and above T_g.

3.2 Change of surface topology of coatings with respect to hygrothermal cyclic test

To examine the coating surface on a microscopic level according to the hygrothermal cycles, the surface roughness of the coatings was monitored by AFM.

AFM images of DGEBA/PA and DGEBA/MXDA coating in terms of hygrothermal cycles are shown in Fig. 5 and 6. The initial surface roughness of DGEBA/PA epoxy coating was much lower than that of DGEBA/MXDA coating. The surface roughness of DGEBA/PA epoxy coating was not altered by hygrothermal cycles. On the other hand, the surface roughness of DGEBA/MXDA epoxy coating was greatly changed by hygrothermal cyclic test. The surface roughness changes of epoxy coatings were described in Table 1.

As a result of AFM examination, it is inferred that the DGEBA/PA epoxy coating was thermally more stable than

Table 1. Surface roughness changes of epoxy coatings cured by different amine based curing agent

Cycle	Average Roughness (nm)	
	DGEBA/PA	DEBGE/MXDA
Before	16.4	244.4
2	12.8	293.6
6	16.0	324.6
8	13.8	454.8

the DGEBA/MADA epoxy coating under hygrothermal ageing.

3.3 Results of corrosion protection by EIS analysis

The corrosion protection of the epoxy coated carbon steels cured by different amine based curing agents was examined by EIS combined with hygrothermal cycling test.[12)-16)]

The EIS results of DGEBA/PA epoxy coated carbon steel is shown in Fig. 7. The impedance modulus log |Z| at 0.1 Hz was measured at 25, 55 and 85 ℃, respectively, as a function of hygrothermal cycles. The impedance modulus decreased from approximately $10^{10}\Omega$ cm^2 to $10^7\Omega$ cm^2 when the temperature of 5 wt % NaCl solution increased to 85 ℃. However, the impedance modulus was recovered to $10^{10}\Omega$ cm^2 when the temperature of 5 wt % NaCl solution dropped 25 ℃. A similar trend was observed, regardless of hygrothermal cycles. The reversibility (R) of impedance modulus of DGEBA/PA epoxy coating was described in Fig. 9 (a). These results were significantly associated with normal state of DGEBA/PA coated sample after hygrothermal cycles as shown in Fig. 10 (a).

Therefore, it is clearly indicated that the impedance

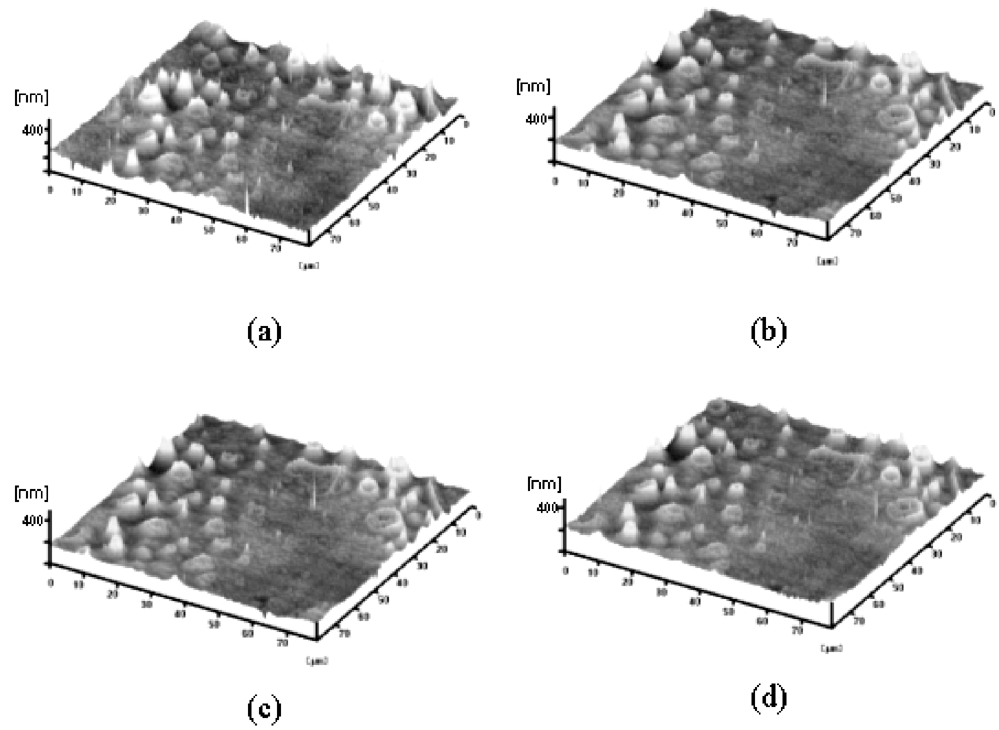


Fig. 5. AFM image of DGEBA/PA coating with hygrothermal cyclic test; (a) initial, (b) After 4 cycles, (c) After 6 cycles and (d) After 8 cycles.

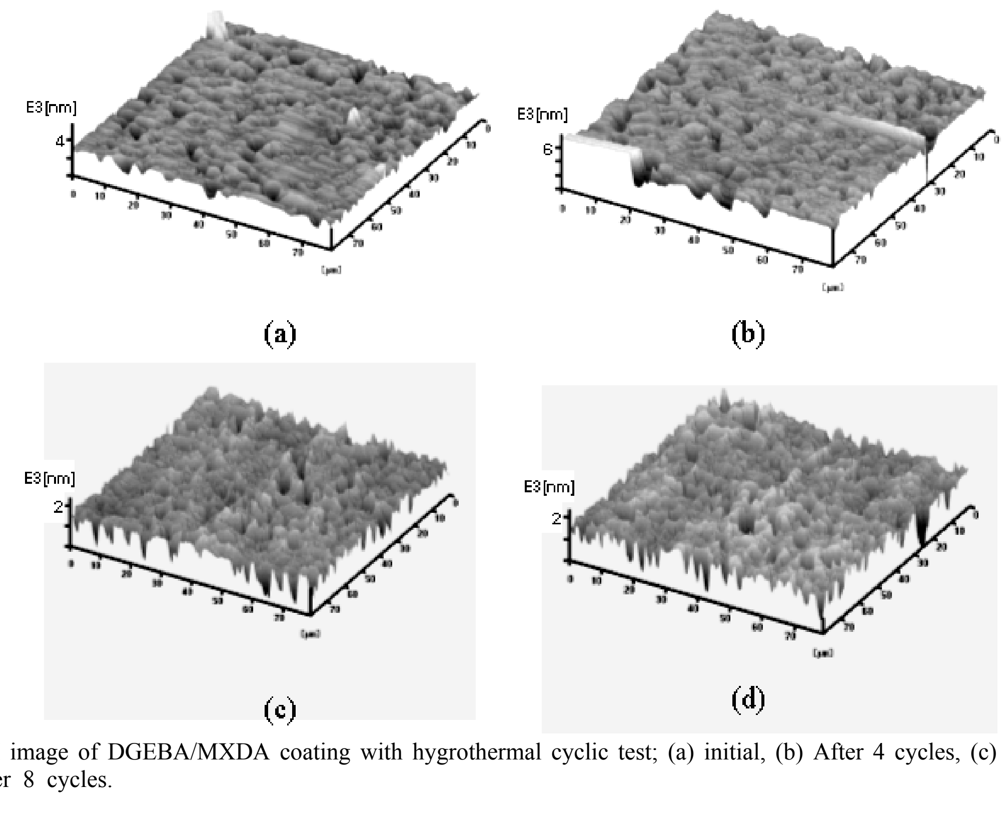


Fig. 6. AFM image of DGEBA/MXDA coating with hygrothermal cyclic test; (a) initial, (b) After 4 cycles, (c) After 6 cycles and (d) After 8 cycles.

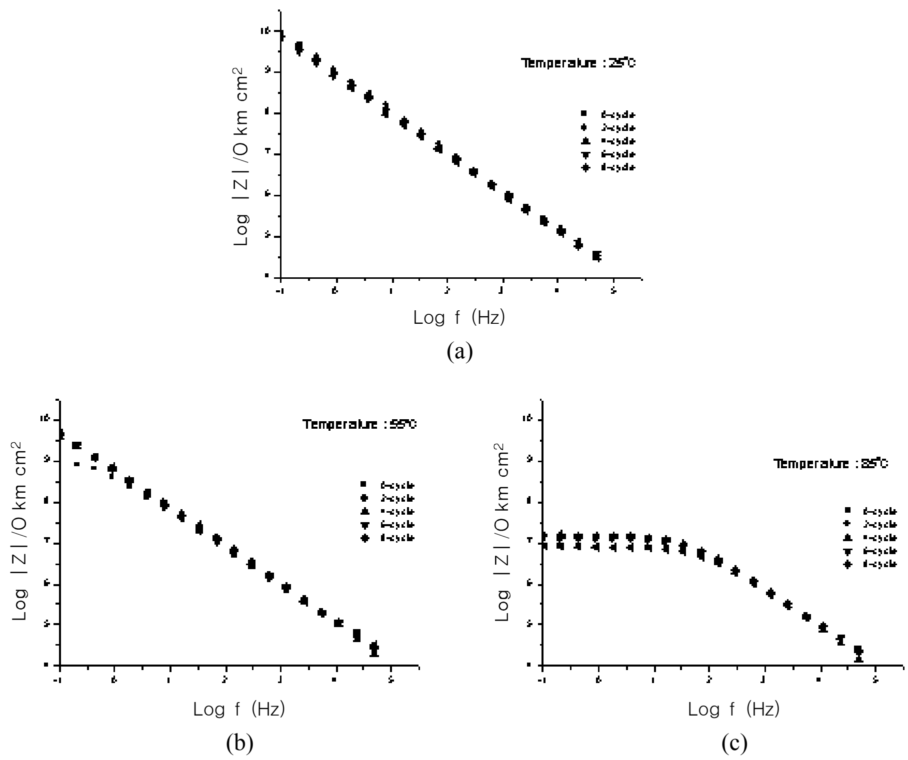


Fig. 7. Impedance modulus |Z| of DGEBA/PA coating at various temperatures with hygrothermal cycles. (a) 25℃ (b) 55℃ and (c) 85℃.

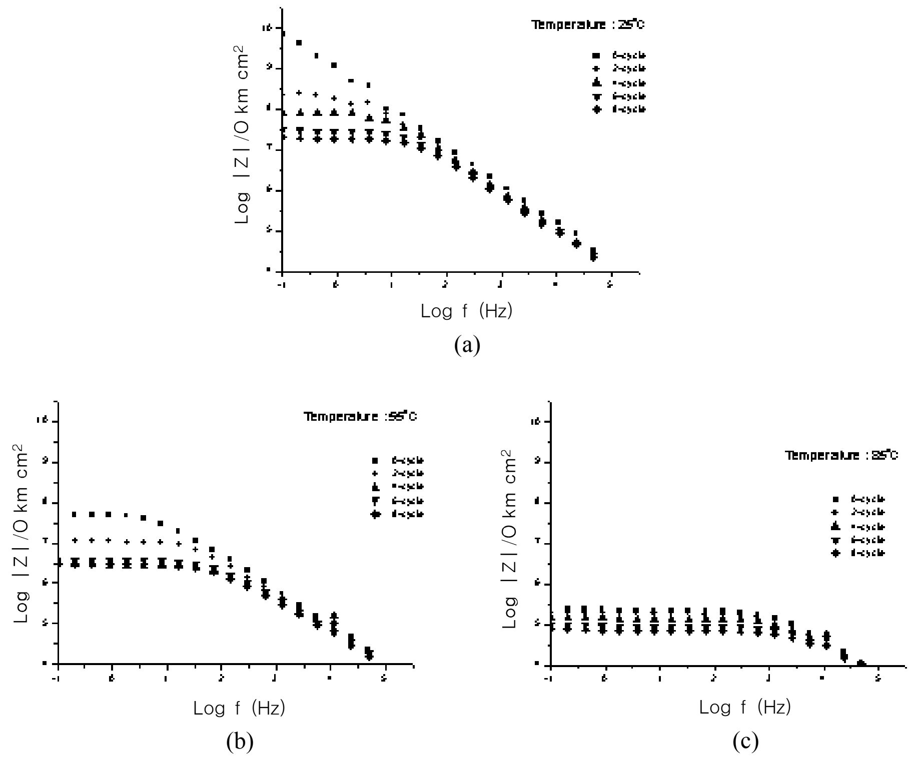
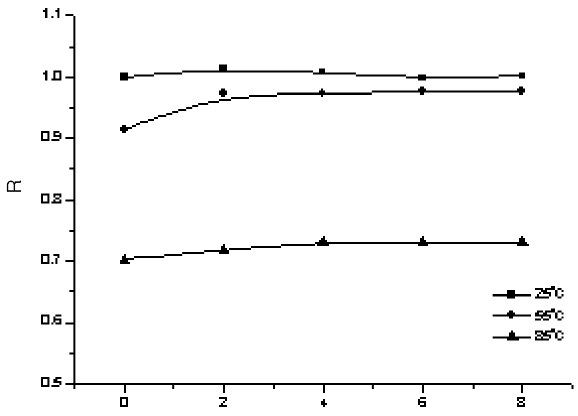
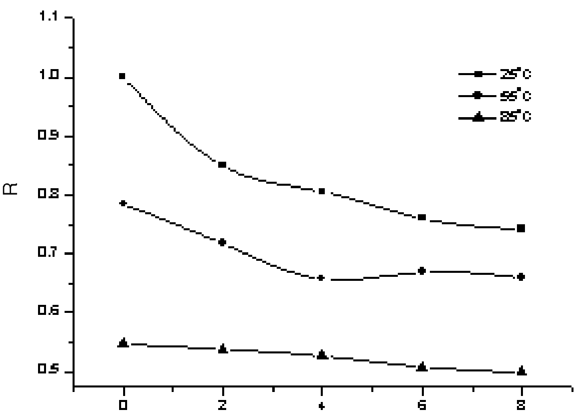


Fig. 8. Impedance modulus |Z| of DGEBA/MXDA coating at various temperatures with thermal cycle runs. (a) 25℃ (b) 55℃ and (c) 85℃.

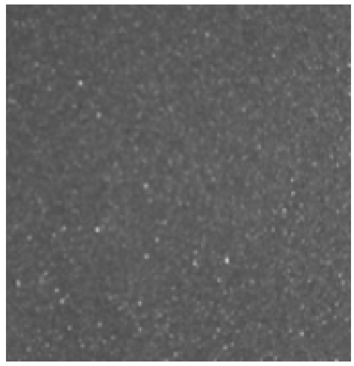


(a)

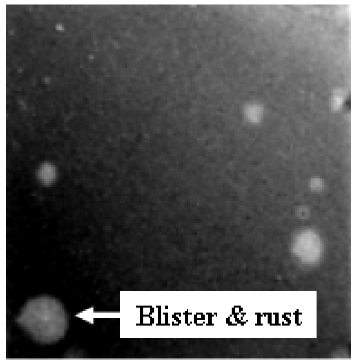


(b)

Fig. 9. Reversibility of impedance modulus at various temperatures with hygrothermal cycles; (a) DGEBA/PA coating and (b) DGEBA/MXDA coating.



(a)



(b)

Fig. 10. Macro photograph of coated carbon steels after 8 hygrothermal cycles; (a) DGEBA/PA coating and (b) DGEBA/MXDA coating.

modulus reversibility of DGEBA/PA epoxy coating is relatively constant in the hygrothermal cyclic test condition. Impedance modulus results is well matched with the observation of corrosion products on the surface of samples (Fig. 10)

On the other hand, DGEBA/MXDA epoxy coated carbon steel showed different corrosion resistance compared with DGEBA/PA epoxy coated carbon steel.

The EIS results of DGEBA/MXDA epoxy coated carbon steel are shown in Fig. 8. The impedance modulus log |Z| at 0.1 Hz was measured at 25, 55 and 85 ℃, respectively, as a function of hygrothermal cycles. Impedance modulus of DGEBA/MXDA epoxy coating at 0.1 Hz decreased from approximately $10^{10}\Omega$ cm^2 to $10^5\Omega$ cm^2. The decreasing rate of impedance modulus was higher than that of DGEBA/PA epoxy coating and impedance modulus at 0.1 Hz was not recovered to initial impedance modulus when the temperature of 5 wt.% NaCl solution return to 25 ℃. The reversibility (R) of impedance modulus of DGEBA/MXDA epoxy coating was described in Fig. 9 (b). These results were closely associated with observation of localized blistering and corrosion product at carbon steel as shown in Fig. 10 (b).

Accordingly, it is clearly observed that the corrosion protection of DGEBA/MXDA epoxy coating is relatively lower than that of DGEBA/PA epoxy coating

4. Conclusions

Conclusions drawn from the work are as follows;

1) The thermal stability of epoxy coating is more appreciable in the epoxy coatings cured by polyamide curing agents becuase DGEBA/PA epoxy coating has high T_g and low coefficient of thermal expansion

2) The surface roughness was changed to high with hygrothermal cycles when epoxy coating was cured by MXDA while the surface roughness of epoxy coatings cured by

polyamide not changed.

3) The impedance modulus of epoxy coating cured by MXDA |Z| at low frequency region was decrease with in hygrothermal cycling test while that of epoxy coating layer cured by polyamide was not decreased.

4) Consequently, the corrosion protection of the epoxy coatings was well matched with their thermal stability being associated with the initiation and growth of blistering and localized corrosion.

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