

# Effects of Curing Agent on the Corrosion Protection of Diglycidyl Ether Bisphenol-A Based Epoxy Coating

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Epoxy coatings were prepared to give a different corrosion protection by reacting it with two different kinds of curing agent, and then effects of the curing agents on the structure, surface hydrophobic tendency, water transport behavior and hence corrosion protection of epoxy coatings were examined using hygrothermal cyclic test, and impedance analysis. In the results of EIS, the corrosion protection of epoxy coating cured by polyamide shows better than epoxy coating cured by polyamide epoxy adduct. It was well agreed with its water transport behavior and hydrophobic tendency.

**Keywords** : epoxy coating; hydrophobic; water diffusivity; hygrothermal test; corrosion

## 1. Introduction

Epoxy is one of the most common coating materials used in severe corrosion environments including marine environment.<sup>1,2)</sup> Due to the hydrophilic chemical groups of cured epoxy structure such as hydroxyl group (-OH), carboxyl group (C=O) and amino group (N-H) that have unpaired electron, epoxy has exhibited the hydrophilic properties by attracting water from the environment<sup>3-6)</sup> to which it is exposed, resulting in a decrease in its protectiveness for metal underneath. Accordingly, there have been a lot of efforts to improve the protectiveness of epoxy coats, considering their material cost and applications, etc. Hydrophobic coating materials such as fluorine<sup>7)</sup> and silicon polymer were introduced for special purposes requiring high corrosion protection, especially as a top coating in heavy duty environments or an anti-fouling coating in ship-building industry. However, the applications of these polymers have been limited due to their bad workability during painting work, poor adhesion and expensive material cost.

In the resent study, electrochemical approaching for coating research was investigated focusing the detecting of defects<sup>8-11)</sup> and few studies on the effects of water sorption on the corrosion protection of coating has been carried out<sup>12-13)</sup>

Shu-Yong Zhang et al<sup>14)</sup> reported the effect of polymeric structure on the corrosion protection of epoxy coatings. They controlled the polymer backbone more hydrophilic and less hydrophilic and they found that the water affinity induced by hydrophilic chemical groups was important factor to determine the corrosion protection of epoxy coatings.

In present study, polyamide and polyamide-epoxy adducts curing agents were considered as curing agent. Those materials are widely used as curing agent for Diglycidyl ether bisphenol-A (DGEBA) epoxy resin which was generally applied to heavy-duty coatings such as ships, bridges and automobiles.

The research objective of present work is to develop an epoxy coat system by curing with polyamide and polyamide-epoxy adducts curing agents which have slightly different chemical structures, and then to examine the effects of the curing agent on the corrosion protection of the epoxy coatings.

## 2. Experimental

### 2.1 Materials

Diglycidyl ether bisphenol-A (DGEBA) was used as base resin and polyamide (PA) and polyamide epoxy adduct (PAEA) were used as epoxy 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.

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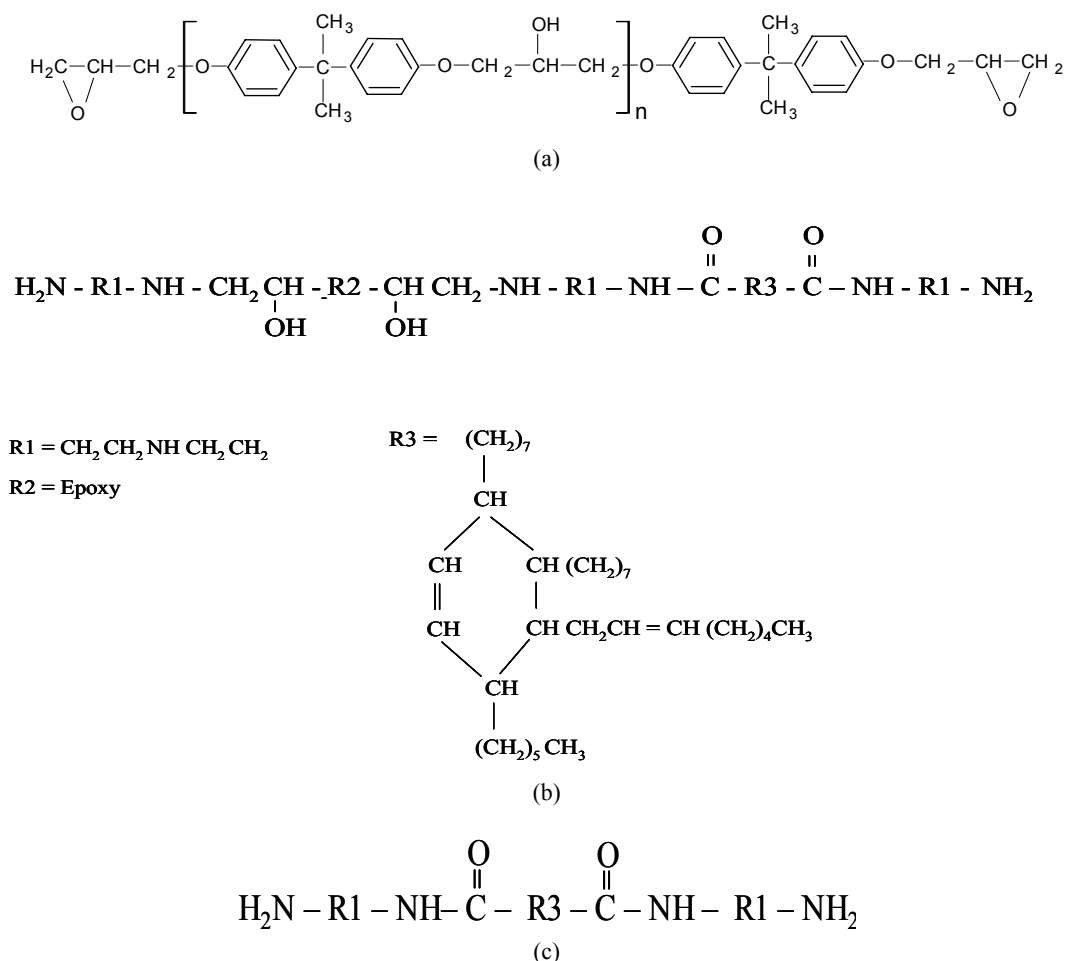


Fig. 1. Molecular structures of epoxy coating system; (a) DEGBA, (b) Polyamide epoxy adduct and (c) Polyamide

Table 1. Mixing ration of resin and curing agent

Blending system	Mixing ratio (wt%)
DGEBA/Polyamide	1/
DGEBA/Polyamide-Epoxy adduct	1/

## 2.2 Preparation of epoxy coating specimens

Epoxy coatings were prepared by mixing DGEBA, PA and PAEA according to the designed mixing ratio as specified in Table 1. The mixtures were vigorously stirred and degassed for 10 min. The epoxy coats were sprayed on steel plate to 100±10 µm thick by an air spray method, and then cured at 25 °C for 4 days followed by post-curing for 4 h at 80 °C. After the curing, the films were used for contact angle measurements.

Carbon steel sheet (30 mm × 30 mm × 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 working electrode to 100±10 µm thick by the air spray method. The coated specimens were then cured in an oven for 4 days at 25 °C, and then post cured for 4 h at 80 °C.

## 2.3 Analysis of surface property

The surface properties of the epoxy system depending on the curing agents was evaluated by measuring the contact angle using a contact angle meter GSA10 (KRÜSS Co. Ltd.) according to the Sessile drop method. The contact angle was measured at 10 seconds after dropping the distilled water.

## 2.4 Electrochemical cell and EIS combined with hydrothermal cyclic test

Hydrothermal cyclic tests were conducted to accelerate

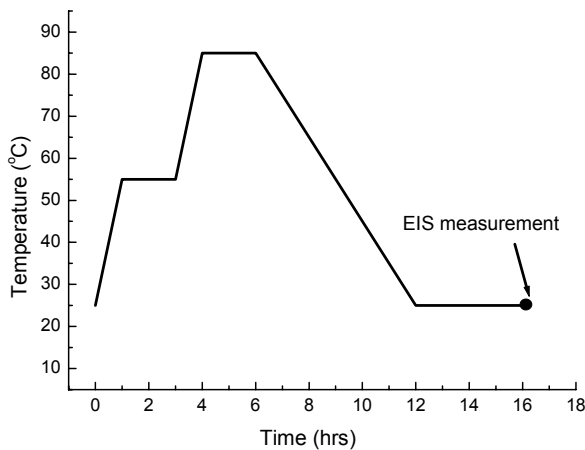


Fig. 2. Heating cycle used in the hydrothermal cyclic test.

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. 2 in which the cooling of specimen from the maximum temperature occurred naturally. Three electrode electrochemical cell consisted of the epoxy coated carbon steel as a working electrode, a saturated calomel reference electrode, and a platinum counter electrode was used to conduct electrochemical impedance spectroscopy (EIS) test at corrosion potential in 5 wt.% NaCl solution. The impedance and capacitance of the modified epoxy coated carbon steel electrode was measured by EIS method. The data were obtained by applying a sine wave of 50 mV amplitude as a function of frequency ranged from 100 kHz to 100 mHz.

### 3. Results and discussion

#### 3.1 Contact angle measurement

A static contact angle was measured on a epoxy coating with PA and PAEA, respectively, and the results were presented in Fig. 3 and Table 2. Evidently, the contact angles on the epoxy coatings cured with PA showed higher than that on the epoxy coatings cured with PAEA. These results clearly indicate that the hydrophobic tendency of the coating surface is more appreciable when the epoxy coating was cured by PA.

#### 3.2 Effects of modifier for water transport behaviors

To investigate the diffusion of water through the epoxy coatings cured with different curing agents, 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<sup>15)-18)</sup> suggested an empirical expression that relates the capaci-

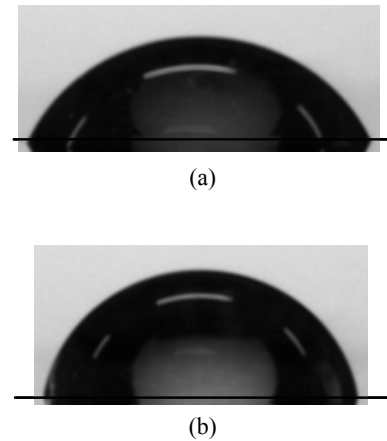


Fig. 3. Effects of curing agent on the contact angle of epoxy coatings: (a) Polyamide epoxy adduct and (b) Polyamide

Table 2. Contact angle measurement of epoxy coatings

Epoxy system	Contact Angle (degree°)
DGEBA/Polyamide	77
DGEBA/Polyamide-Epoxy adduct	45

tance of a coating to the volume fraction of water absorbed into the coating, which was expressed by Eq. (1)

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

where,  $V_t$  is volume fraction of absorbed water at time  $t$ ,  $C_0$ ,  $C_t$ , are the capacitances of an organic coating at time  $t = 0$  and at time  $t$ , respectively and  $\epsilon_{H_2O}$  is the dielectric constant of water (80 at  $T = 20^\circ\text{C}$ ). Further, the diffusion coefficient of water into an organic coating can be calculated by Eq. (2) in which [slope] is that at the initial stage of  $\ln C_c - \sqrt{t}$  plot, called "the initial slope method",<sup>19),20)</sup>

$$D = \frac{L^2 \pi}{4} [\text{slope}]^2 \quad (2)$$

Where  $C_c$  is the capacitance of the organic coating, and  $L$  is thickness of the coating. The capacitance of a coating at the frequency of 1 kHz was selected for the calculation of diffusion coefficient of water through the coating in this work. The  $\ln C_c - \sqrt{t}$  curve of an organic coating can be divided into two typical stages. At the first stage, the capacitance of a coating increases linearly with immersion time, indicating that the water may permeate into the coating through pores formed by a solvent evaporation, free

volume or space between cross-linked chains formed by a curing reaction. At the second stage or after a certain time of immersion, the capacitance of the coating reaches a constant value, indicating that the water uptake into the coating has been saturated.

Fig. 4 shows  $\ln C_c - \sqrt{t}$  curve of the epoxy coating cured with PA. Diffusion coefficient of water into an epoxy coating was calculated from the slope of  $\ln C_c - \sqrt{t}$  curve using Eq. (2), and volume fraction of water uptake was calculated by equation (1). The capacitance of dry coating,  $C_0$ , was determined by extrapolation of  $\ln C_c - \sqrt{t}$  curves at  $t$

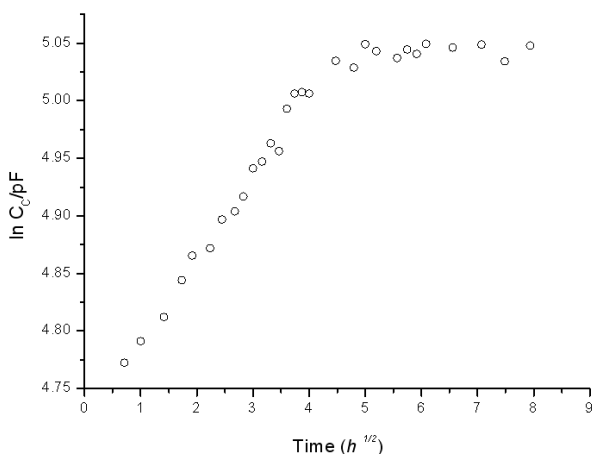


Fig. 4.  $\ln C_c - t^{1/2}$  curve for epoxy coating cured by Polyamide epoxy adduct, measured in 5.0 wt% NaCl solution.

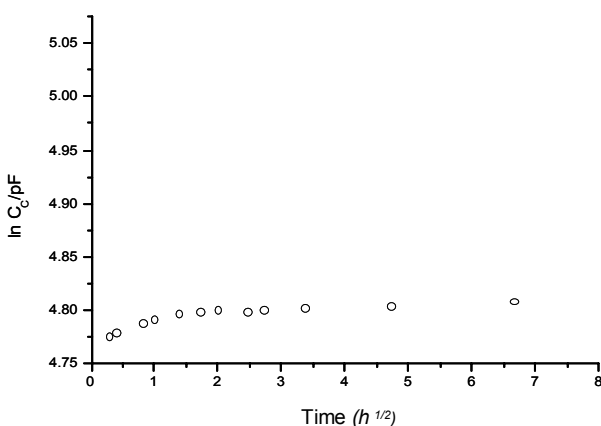


Fig. 5.  $\ln C_c - t^{1/2}$  curve for epoxy coatings cured by Polyamide epoxy adduct, measured in 5.0 wt% NaCl solution.

= 0. The diffusion coefficient of water and the water uptake for the epoxy coating with PA was calculated to be  $6.4 \times 10^{-8} \text{ cm}^2/\text{s}$  and 0.74 volume % at 25 °C, respectively. Fig. 5 shows  $\ln C_c - \sqrt{t}$  curves for the epoxy coatings cured with PAEA. The calculated diffusion coefficient of water in the epoxy coating with PAEA was calculated to be  $99.4 \times 10^{-8} \text{ cm}^2/\text{s}$  and 6.15 volume % at 25 °C, respectively. The calculated values of water diffusion coefficient and water uptake were given in Table 3. These results clearly demonstrate that the water diffusion coefficients in the epoxy coatings cured with PA is much lower than that of the epoxy coating cured with PAEA, and hence the water uptake into the coatings with PA is much less than that into the epoxy coating with PAEA. These results are confirming that diffusion coefficient of water of epoxy coatings is well agreed with results of its surface hydrophobic tendency.

### 3.3 Effects of modifier on corrosion protectiveness from the EIS results

The corrosion protection of the modified epoxy coated steel was examined by EIS combined with hygrothermal cycling test.<sup>21)-26)</sup> Fig. 6 shows EIS spectrum measured for carbon steel coated with the epoxy cured with PAEA as a function of cycle in the hygrothermal test. Impedance modulus of  $\log |Z|$  at 0.1 Hz decreased even after one cycle of the hygrothermal test, and then continues to re-

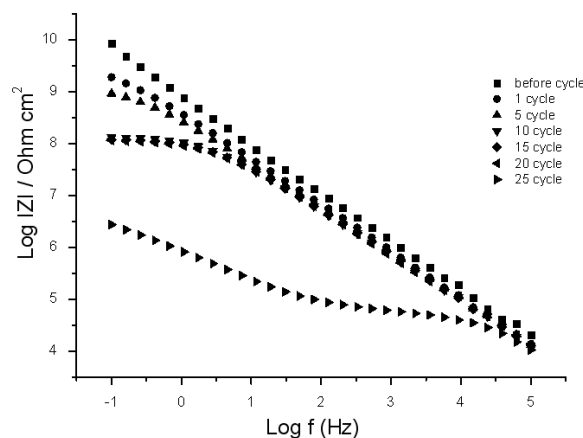


Fig. 6. EIS spectra in Bode plot for epoxy coating cured by Polyamide epoxy adduct

Table 3. Water transport behaviors of epoxy coatings

Blending system	Diffusion Coefficient ( $\times 10^{-8}$ , $\text{cm}^2/\text{s}$ )	Volume Fraction of Water Uptake (Vol %)
DGEBA/Polyamide	6.4	0.74
DGEBA/Polyamide-Epoxy adduct	99.4	6.15

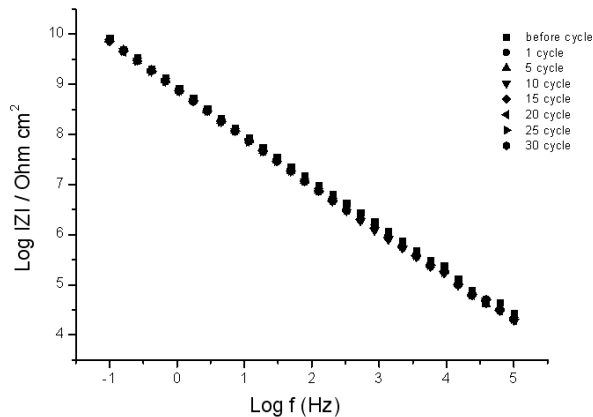


Fig. 7. EIS spectra in Bode plot for epoxy coating cured by Polyamide

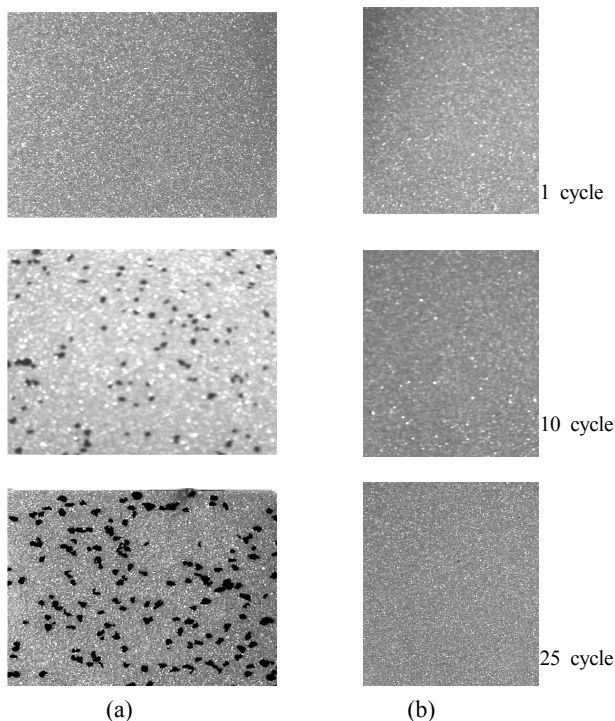


Fig. 8. Photographs of localized corrosion occurred on epoxy coated carbon steel after 25 hydrothermal cycles. The epoxy coatings were cured by different curing agents; (a) Polyamide epoxy adduct, (b) Polyamide

duce with cycling, which was associated with an occurrence of corrosion at carbon steel, as shown in Fig. 8.

Fig. 7 shows the EIS spectrum as a function of cycle in the hydrothermal test for carbon steel coated with the epoxy cured with PA. Evidently, the impedance modulus  $|Z|$  at 0.1 Hz showed the constant impedance modulus at 0.1 Hz even after 30 cycles, suggesting that corrosion did not occur on the coated carbon steel as shown in Fig. 8.

Fig. 8 shows effects of curing agent type on the corrosion morphology on the carbon steel coated with epoxy coatings cured with two different curing agents. Evidently, localized corrosion occurred by an electrochemical reaction of carbon steel with water that had been transported to steel surface by diffusion through the coating layer during the hydrothermal test. When compared the results of water transport behaviors through the coatings, it is evident that the epoxy coating cured by PA with lower diffusion coefficient or lower water uptake caused no corrosion attack on carbon steel. Further, the decrease in the impedance modulus  $|Z|$  at low frequency region with cycling in hydrothermal test for the epoxy coatings, shown in Fig. 6 to Fig. 7, associated with initiation and growth of localized corrosion on carbon steel as well as the increase in water uptake into the coating.

#### 4. Conclusions

Conclusions drawn from the work are as follows;

- (1) The hydrophobic tendency of the coating surface is more appreciable when the epoxy coating was cured by PA.
- (2) Water diffusivity and water uptake into the epoxy coating was much lower than that into the epoxy coating cured by PAEA.
- (3) The decrease in the impedance modulus  $|Z|$  at low frequency region with cycling in hydrothermal test for epoxy coatings was associated with the initiation and growth of localized corrosion on carbon steel. The size of corrosion spot and its occurrence density of the PAEA cured epoxy coated carbon steel generally increased with thermal cycles, confirming that corrosion protection of the epoxy coating is well agree with its water transport behavior.

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