Effects of Surface Modification with Amino Terminated Polydimethylsiloxane(ATP) on the Corrosion Protection of Epoxy Coating

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An epoxy coating was designed to give a hydrophobic property on its surface by modifying it with three types of Amino Terminated Polydimethylsiloxane (ATP), and then effects of the modification on the structure, surface hydrophobic tendency, water transport behavior and hence corrosion protectiveness of the modified epoxy coating were examined using FT-IR spectroscopy, hydrothermal cyclic test, and impedance test. The surface of epoxy coating was changed from hydrophilic to hydrophobic property due primarily to a phase separation tendency between epoxy and modifier by the modification. The phase separation tendency is more appreciable when modified by ATP with higher molecular weight ATP at higher content. Water transport behavior of the modified epoxy coating decreased more in that with higher hydrophobic surface property. The resistance to localized corrosion of the modified epoxy coated carbon steel was well agreed with its water transport behavior and hydrophobic tendency.

Keywords : epoxy coating; hydrophobic; water diffusivity; hydrothermal test; corrosion

1. Introduction

Epoxy is one of the most common coating materials used in severe corrosion environments including marine environment.[1),2)] 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[3)-6)] 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[7)] 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 shipbuilding industry. However, the applications of these polymers have been limited due to their bad workability during painting work, poor adhesion and expensive material cost.

A blending technology combining hydrophilic polymer with hydrophobic polymer may produce an attractive coat-

ing system having both high corrosion protection and good adhesion. In fact, a reactive blending of poly [(3-amino-propyl) methylsiloxane](PAMS) and epoxy has been attempted to improve the impact resistance of composite materials and adhesives by separating PAMS from the epoxy phase as a spherical shape.[8)-10)] In other approach, J.C. Cabanelas et al made an epoxy system by adding PAMS as a curing agent rather than as a modifier,[10)] and confirmed that the water absorption of the epoxy was significantly decreased due to the change from hydrophilic to hydrophobic properties of epoxy coating. However, the introduction and application of amino substituted polydimethylsiloxane as a surface modifier for epoxy coating was rarely reported in the literatures. T. Kasemura et al examined the surface modification of epoxy from hydrophilic to hydrophobic by blending aminopropyl terminated polydimethylsiloxane with epoxy.[11),12)] However, the effects of the surface modifications on the corrosion protection of epoxy have rarely been investigated.

The research objective of present work is to develop an epoxy coat system by modifying its surface with amino terminated polydimethylsiloxane that is hydrophobic and immiscible with epoxy, and then to examine the effects of the surface modification on the corrosion protection of the modified epoxy coatings.

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$$CH_3 \quad CH_3 \quad CH_3$$
$$H_2N\text{-}(CH_2)_3\text{-}Si\text{-}O\text{-}(Si\text{-}O)_n\text{-}Si\text{-}(CH_2)_3\text{-}NH_2$$
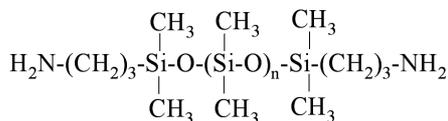$$CH_3 \quad CH_3 \quad CH_3$$

Fig. 1. Molecular structure of ATP.

2. Experimental

2.1 Materials

Diglycidyl ether bisphenol-A (DGEBA) and polyamide epoxy adduct (PAEA) were used as epoxy curing agents. Three types of amino terminated polydimethylsiloxane (ATP) with different number of average molecular weight of 1,900 g/mol (ATP 1), 4,500 g/mol (ATP 2) and 14,000 g/mol (ATP 3), respectively, were used as surface modifiers. Toluene was used as a solvent of the coatings. The molecular structures of ATP were shown in Fig. 1

2.2 Preparation of modified epoxy specimens

Modified epoxy coatings were prepared by mixing DGEBA, PAEA and ATP 1, ATP2 and ATP3 according to the designed ratio as specified in Table 1. The mixtures were vigorously stirred and degassed for 10 min during blending. The modified epoxy coats were sprayed on polypropylene 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 removed for further tests such as measurements of contact angle and FT-IR.

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 modified 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 modification

FT-IR spectroscopy scanning was conducted from 4000 to 650 cm^{-1} on the top and bottom parts of the epoxy coating modified with different contents of ATP 1, ATP 2 and ATP 3. ATR (Attenuated Total Reflection) method was applied at 45° of IR beam, with the penetration depth of beam into the coating layer being about 1.47 μm at 1000 cm^{-1}.

Distribution of the modifier (ATP) in the modified epoxy coating was analyzed by measuring the Si peak intensity by ATR mode of FT-IR (JASCO 680 plus, USA) since Si is contained only in ATP. Fig. 3 shows IR spectrum of pure ATP in which the peak at 1010 cm^{-1}, at 800 cm^{-1}, and at 1260 cm^{-1}, respectively, are those for Si-O-Si stretching vibration, Si-C stretching and rocking, and CH$_3$ symmetric deformation of Si- CH$_3$, respectively. All of these peaks were used to characterize the distribution of the modifier.

2.4 Electrochemical cell and EIS combined with hydrothermal cyclic test

Hydrothermal 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. 4 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 100 mV amplitude as a function of frequency ranged from 100 kHz to 100 mHz.

3. Results and discussion

3.1 Modifier distribution and surface modification. (FT-IR Analysis)

Fig. 2(a) and (b) shows IR spectra measured on top and bottom, respectively, of the epoxy coatings modified with ATP 1 as a function of ATP 1 content. Peaks 1, 2, and 3 marked in Fig. 2 are those characterizing the epoxy without modifier such as ATP 1, ATP 2 and ATP 3 ; the aliphatic C-O stretching vibration at 1040 cm^{-1}, hydrogen atoms of para-disubstitued aromatic bending at 820 cm^{-1}, and phenyl O stretching vibration at 1250 cm^{-1}. These three peaks were used as those of reference to identify the distribution of modifier in the modified epoxy coatings. It is evident from Fig. 2(a) and (b) that IR spectra of the epoxy coatings modified with ATP1 are almost similar each other, irrespective of the ATP1 content, suggesting that the modifier ATP1 is uniformly distributed from the bottom to the top of the coatings

Fig. 3(a) and (b) shows IR spectra measured on the top and bottom layers as a function of ATP 2 content,

(a)

(b)
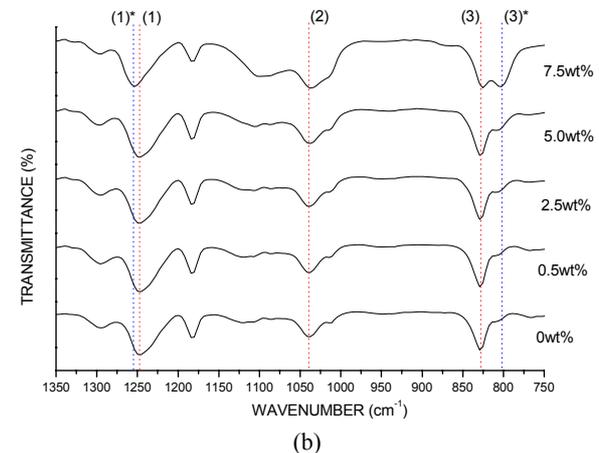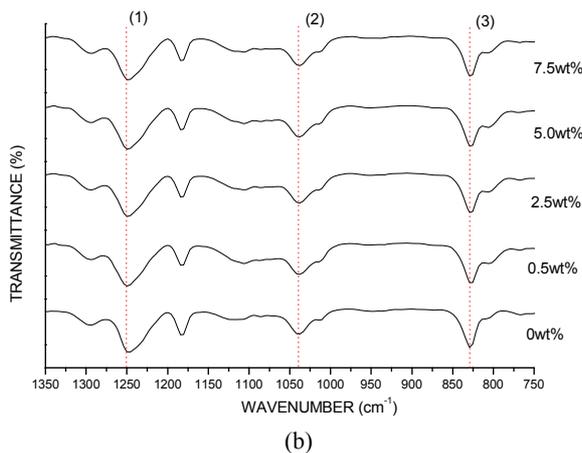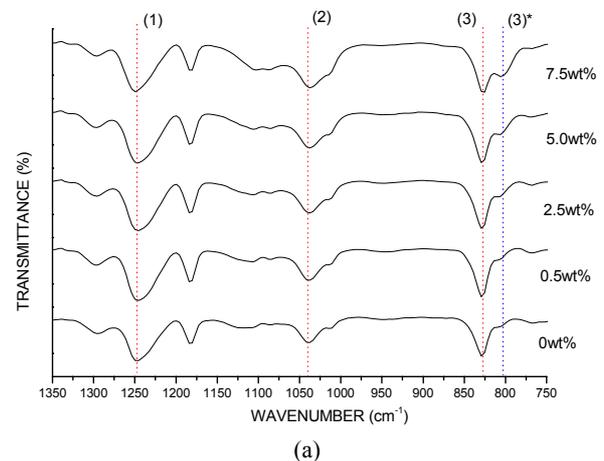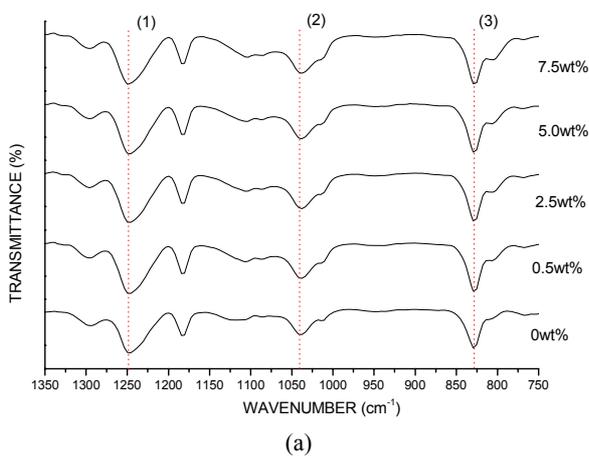
Fig. 2. IR spectra of epoxy coatings modified with various contents of ATP 1: (a) coating bottom layer and (b) coating top layer.

[(1)] Phenyl -O- stretching: 1250 cm^{-1}
[(2)] Aliphatic C-O stretching vibration: 1040 cm^{-1}
[(3)] Bending of two adjacent hydrogens of para -Disubstituted aromatic: 820 cm^{-1}

respectively, for the epoxy coatings modified with ATP 2. In addition to the reference peaks 1, 2, and 3, new peaks marked 1*, 2* and 3*, characterizing the presence of Si in the modifier, were appeared in the IR spectrum ; Si-O-Si stretching vibration at 1010 cm^{-1}, Si-C stretching and rocking at 800 cm^{-1}, and CH$_3$ symmetric deformation of Si- CH$_3$ at 1260 cm^{-1}. It is evident from the IR spectra for the top and bottom layers shown in Fig. 3(a) that the peak 3 was shifted to the peak 3*, respectively, at ATP2 content higher than 7.5 wt. %. These results clearly demonstrated that the modifier ATP2 is distributed in the top layer and bottom layer of the modified epoxy coatings.

The phase separation tendency between epoxy and modifier is more appreciable in the epoxy coatings modified with higher molecular weight such as ATP3 as con-

(a)

(b)

Fig. 3. IR spectra of epoxy coatings modified with various contents of ATP 2: (a) coating bottom layer and (b) coating top layer.

firmed in Fig. 4 (a) and (b). Evidently, the shift of peaks 1, 3 to peaks 1* and 3* occurred at the ATP3 content greater than 2. 5 wt. % on the top layer of the coating, whereas peaks 1*, 2* and 3* were appeared in the bottom layer ATP3 content greater than 7. 5 wt.% indicating that the modifier ATP3 is distributed dominantly on the top layer of the coating.

3.2 Effects of modifier for water transport behaviors

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[16)-19)] 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 Eq. (2)

(a)

(b)
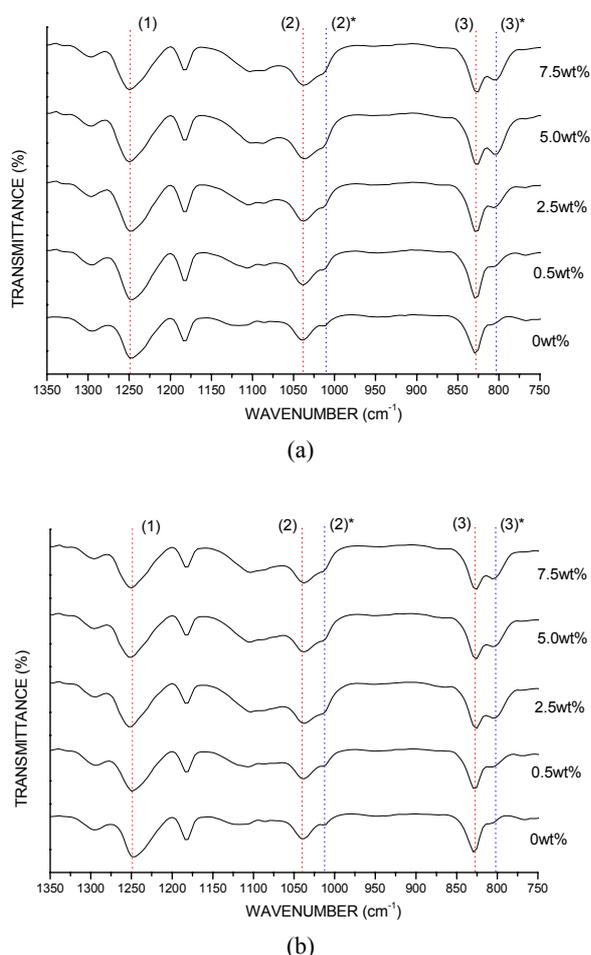
Fig. 4. IR spectra of epoxy coatings modified with various contents of ATP 3: (a) coating bottom layer and (b) coating top layer.

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

where, V_t is volume fraction of absorbed water at time t, C_o, C_t are the capacitances of an organic coating at time $t = 0$ and at time $= t$, respectively and ε_{H_2O} is the dielectric constant of water (80 at $T = 20\,°C$). Further, the diffusion coefficient of water into an organic coating can be calculated by Eq. (3) in which [slope] is that at the initial stage of $\ln C_C$ - $\sqrt{t}$ plot, called "the initial slope method",[20),21)]

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

where C_∞ is the capacitance of the organic coating at a saturated state, and L is thickness of the coating. The capacitance of a coating at the frequency of 1 kHz was se-

Table 1. Volume fraction of water uptake at the saturation equilibrium and Water diffusion coefficients calculated with Eq. (1) and Eq. (2)

Blending system	Diffusion Coefficient ($\times 10^{-8}$, cm^2/s)	Volume Fraction of Water Uptake (Vol %)
Epoxy	99.4	6.15
ATP 1 (0.5 wt%)	64.7	5.55
ATP 1 (2.5 wt%)	46.9	4.34
ATP 1 (5.0 wt%)	34.0	3.81
ATP 1 (7.5 wt%)	33.4	3.34
ATP 2 (0.5 wt%)	62.0	5.24
ATP 2 (2.5 wt%)	50.2	4.96
ATP 2 (5.0 wt%)	32.0	3.24
ATP 2 (7.5 wt%)	25.8	3.21
ATP 3 (0.5 wt%)	59.1	5.05
ATP 3 (2.5 wt%)	44.1	4.20
ATP 3 (5.0 wt%)	31.6	3.23
ATP 3 (7.5 wt%)	20.8	3.02

lected 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.

The calculated values of water diffusion coefficient and water uptake were given in Table 1. These results clearly demonstrate that the water diffusion coefficients in the epoxy coatings modified with either ATP 1 or ATP 2 or ATP3 are much lower than that of the pure epoxy coating, and hence the water uptake into the modified coatings is much less than that into the pure epoxy coating. The effects of modification on the retardation of water transport is more appreciable in the coating modified with greater molecular weight such as ATP3 at higher modifier content.

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 hydrothermal cycling test. Fig. 5 shows EIS spectrum measured for the unmodified epoxy coated on steel as a function of cycle in the hydrothermal test. Impedance modulus of log |Z| at 0.1 Hz decreased even after one cycle of the hydrothermal test, and then continues to reduce with cycling,
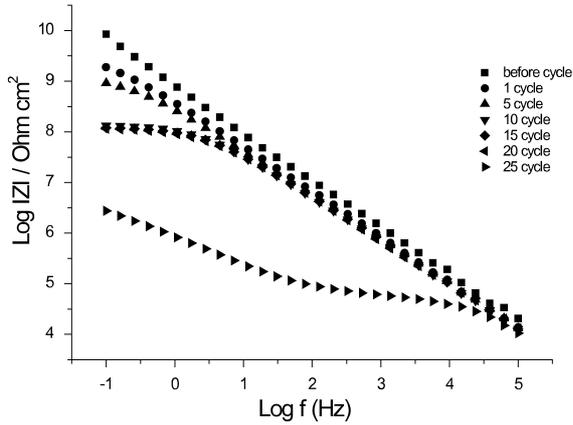
Fig. 5. EIS spectra in Bode plot for epoxy coating without modification according to hygrothermal cycle.

which was associated with an occurrence of corrosion at carbon steel, as will be shown shortly.

Fig. 6 shows the EIS spectrum as a function of cycle in the hydrothermal test for carbon steel coated with the epoxy modified with ATP 1. Evidently, the impedance modulus |Z| of 0.5 wt% of ATP 1 at 0.1 Hz was dropped to a low value after 30 cycles. 2.5 wt% of ATP 1 at 0.1 Hz was dropped to a low value after 39 cycles. However, 5.0 wt% and 7.5 wt% of ATP 1 showed the less drop rate of impedance modulus at 0.1 Hz after 39 cycles.

Fig. 7 and 8 show the EIS spectrum as a function of cycle in the hydrothermal test for carbon steel coated with the epoxy modified with ATP 2. The tendency of impedance modulus |Z| drop at 0.1 Hz was very similar to the case of ATP1.
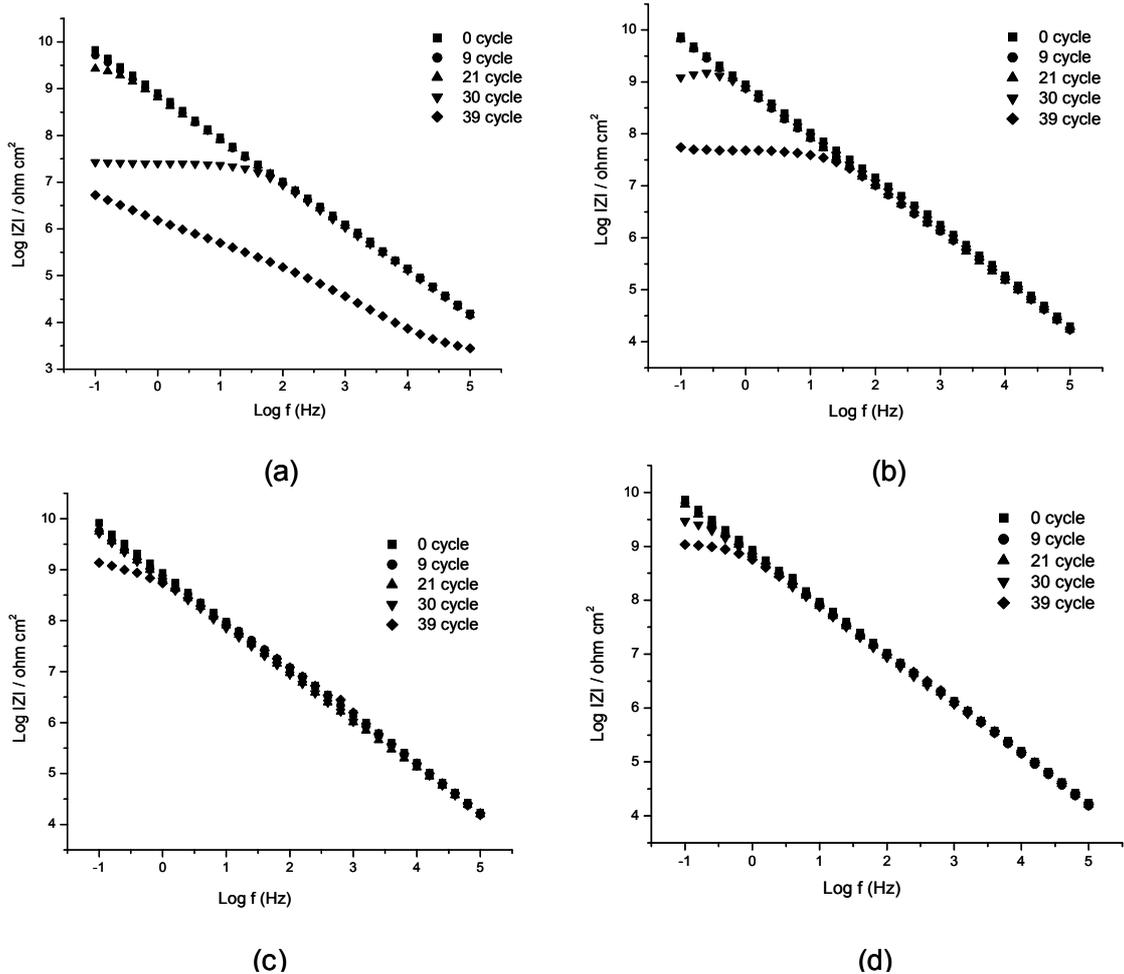

Fig. 6. EIS spectra in Bode plot for epoxy coating modified with various contents of ATP1 according to hygrothermal cycle: (a) 0.5 wt% (b) 2.5 wt% (c)5.0 wt% (d) 7.5 wt%.

Fig. 7. EIS spectra in Bode plot for epoxy coating modified with various contents of ATP2 according to hygrothermal cycle: (a) 0.5 wt% (b) 2.5 wt% (c)5.0 wt% (d) 7.5 wt%.

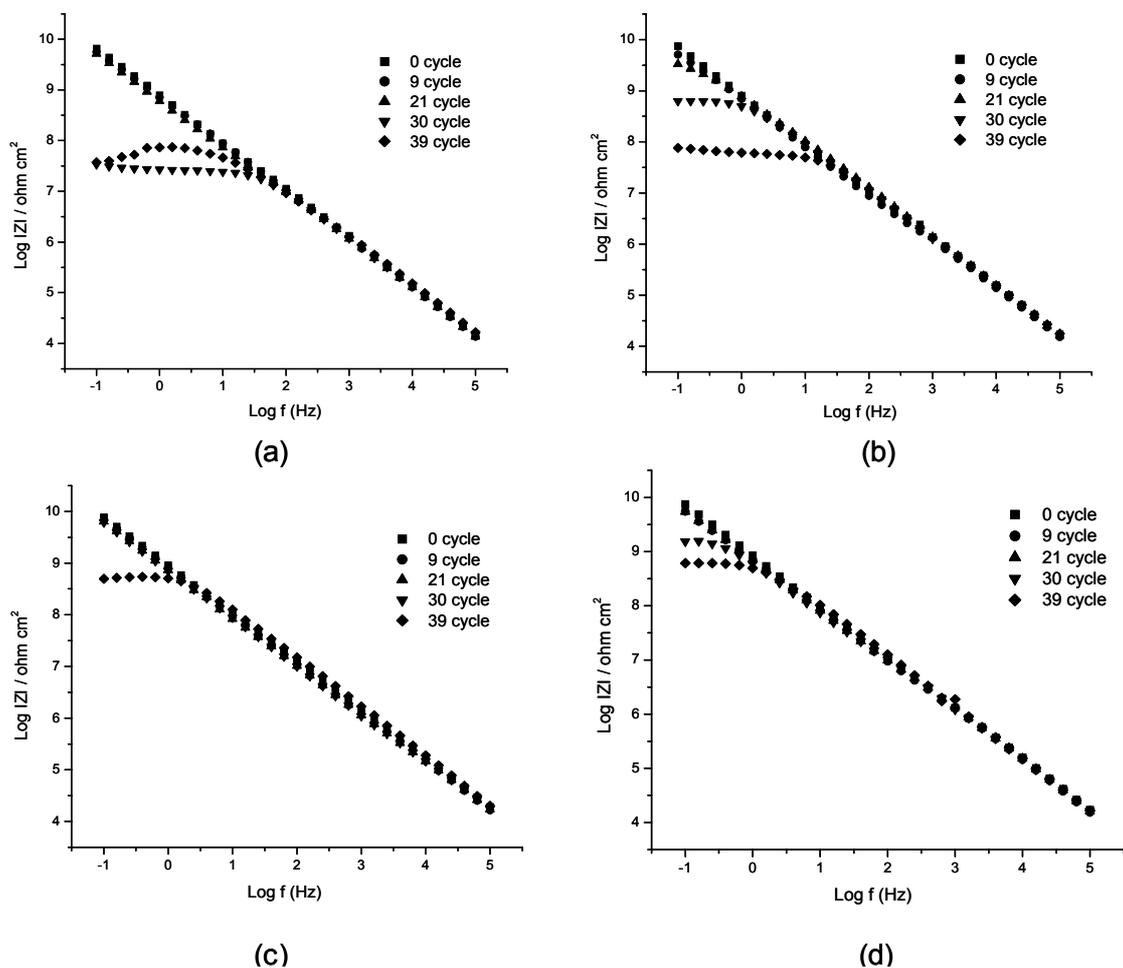## 4. Conclusion

An epoxy coating system was designed to give hydrophobic properties on its surface by modifying the epoxy with three different amino terminated polydimethylsiloxane (ATP) depending on molecular weight, and then we examined the effects of the surface modification on the structure including phase separation between top and bottom of coating, hydrophobic surface properties, water transport behaviors, EIS, and corrosion protection of the modified epoxy coatings. Conclusions drawn from the work are as follows;

1) The phase separation tendency between epoxy and modifier in the modified epoxy coating is more appreciable in the epoxy coatings modified with higher molecular weight such as ATP3

2) Water diffusivity and water uptake into the epoxy coatings modified with ATP were much lower than those

into the pure epoxy coating. The effects of modification on the retardation of water transport are more appreciable in the coating modified with greater molecular weight such as ATP3 at higher modifier content.

3) The decrease in the impedance modulus |Z| at low frequency region with cycling in hydrothermal test for epoxy coatings was associated with the molecular weight of modifier or the modifier content, confirming that corrosion protectiveness of the modified epoxy coating is well agree with its water transport behavior.

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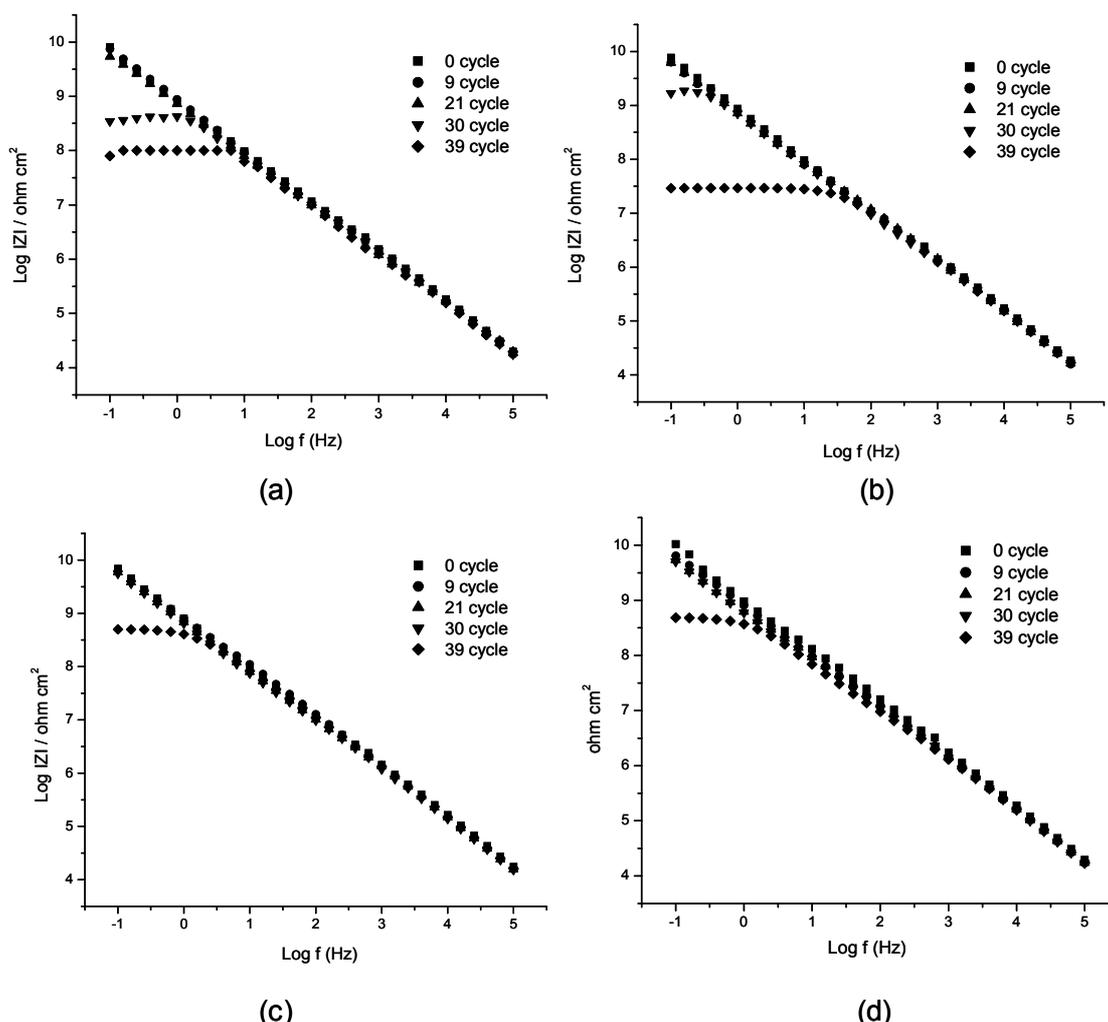
Fig. 8. EIS spectra in Bode plot for epoxy coating modified with various contents of ATP3 according to hygrothermal cycle: (a) ES2-1: 0.5 wt% (b) ES2-2: 2.5 wt% (c) 5.0 wt% (d) 7.5 wt%.

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