Effects of surface modification with hydroxyl terminated polydimethylsiloxane on the corrosion protection of polyurethane coating

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Polyurethane coating was designed to give a hydrophobic property on its surface by modifying it with hydroxyl terminated polydimethylsiloxane and then effects of surface hydrophobic tendency, water transport behavior and hence corrosion protectiveness of the modified polyurethane coating were examined using FT-IR/ATR spectroscopy, contact angle measurement and electrochemical impedance test. As results, the surface of polyurethane coating was changed from hydrophilic to hydrophobic property due primarily to a phase separation tendency between polyurethane and modifier by the modification. The phase separation tendency is more appreciable when modified by polydimethylsiloxane with higher content. Water transport behavior of the modified polyurethane coating decreased more in that with higher hydrophobic surface property. The decrease in the impedance modulus |Z| at low frequency region in immersion test for polyurethane coatings was associated with the water transport behavior and surface hydrophobic properties of modified polyurethane coatings. The corrosion protectiveness of the modified polyurethane coated carbon steel generally increased with an increase in the modifier content, confirming that corrosion protectiveness of the modified polyurethane coating is well agreed with its water transport behavior.

Keywords : polysiloxane, corrosion protection, EIS, polyurethane, FT-IR

1. Introduction

Organic coatings are widely used to give aesthetic appearance and protection from the destructive environments like corrosion. Among them corrosion protectiveness of coatings is very important because coated substrates are frequently exposed to severe circumstance such as water, chemical solution, biological deterioration, UV-radiation, and mechanical damage. Generally, coating applies to both interior and exterior area and the protection performance of coating on substrate is depends on their barrier performance, adhesion performance between coating and substrate. Basically, there are two typical corrosion protectiveness mechanisms of coatings. The first mechanism is physical barrier which isolate the substrate from corrosive environment and second one is inhibition of corrosion using reactive pigments or inhibitors.

Polyurethanes coating are widely used in industrial application because of their excellent weather stability, good chemical resistance, flexibility and long service life.

Polyurethanes coatings are produced by the chemical reaction from polyisocyanates and polyols. The main application is for top coats and clear coats due to its excellent weather stability.

Cabanelas et al. investigated an epoxy system by adding poly[(3-aminopropyl)methylsiloxane] PAMS as a curing agent [1], and reported that the water absorption of the epoxy was significantly decreased due to the change from hydrophilic to hydrophobic properties of epoxy coating. Kasemura et al. studied the surface modification of epoxy by blending aminopropyl terminated polydimethylsiloxane and examined the surface properties changed from hydrophilic to hydrophobic.[2-3] In our previous study, epoxy coatings modified with amino branched polydimethylsiloxane and amino terminated polydimethylsiloxane were designed to give a hydrophobic property on its surface by modifying it with two kinds of amino substituted polydimethylsiloxane, and then effects of the modification on the structure, surface hydrophobic tendency, water transport behavior and hence corrosion protectiveness of the modified epoxy coatings were examined.[4-6] From the examination, improvement of corrosion protectiveness was observed when epoxy coating is modified by amino substituted polydimethylsiloxane.

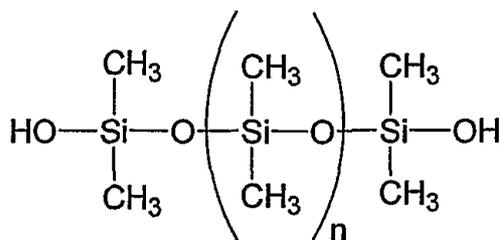[†] Corresponding author: myshon@pknu.ac.kr

Fig. 1. Molecular structure of hydroxyl terminated polydimethylsiloxane (HTPS).

However, the introduction and application of functionalized polydimethylsiloxane as a surface modifier for polyurethane coating was rarely reported.

The research objective of present work is to develop an polyurethane coat system by modifying its surface with hydroxyl terminated polydimethylsiloxane that is hydrophobic and then to examine the effects of the surface modification on the corrosion protectiveness of the modified polyurethane coatings

2. Experimental

2.1. Materials

Acrylic based Polyol (#142850, supplied by Chokwang Paint) and Hexamethylene diisocyanate (HDI, Desmodur N3300) were used as resin and curing agents for polyurethane coating. Two types of hydroxyl terminated polydimethylsiloxane (HTPS) were used as surface modifiers. The number of average molecular weight of HTPS was 2,000 g/mol (HTPS1) and 77,000 g/mol (HTPS2), respectively. Xylene was used as a solvent of the coatings. The molecular structures of HTPS was shown in Figs. 1.

2.2. Preparation of modified polyurethane specimens

Modified polyurethane coatings were prepared by mixing with polyol, HDI and HTPS1 and HTPS2 according to the designed ratio as specified in Table 1. The mixtures were vigorously stirred and degassed for 10 min during blending. The modified polyurethane coats were sprayed on polypropylene plate to 100 ± 10 μm thick by an air spray method, and then cured at 80 °C for 2 h followed
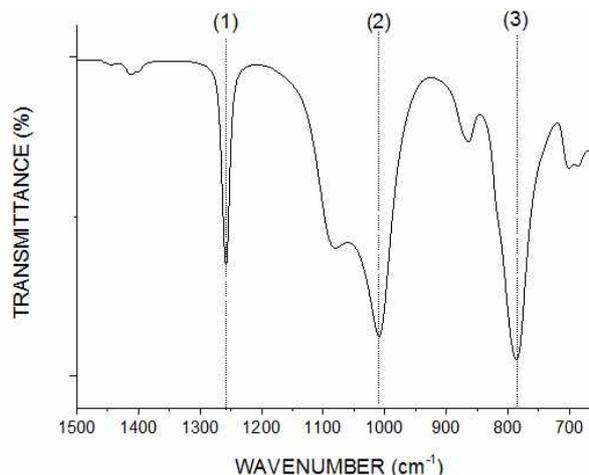
Fig. 2. IR spectrum of HTPS in which functional peaks marked are as follows: (1) CH3 symmetric deformation of Si–CH3: 1260 cm^{-1}, (2) Si–O–Si stretching vibration: 1010 cm^{-1}, and (3) Si–C stretching and rocking: 790 cm^{-1}.

by post-curing for 1 day at 25 °C. After the curing, the films were used for further tests such as contact angle measurement and FT-IR analysis.

For electrochemical impedance spectroscopy (EIS) test, carbon steel (150 mm × 75 mm × 3 mm) was used as a working electrode. Surface of the working electrode was pretreated by steel grit blasting, 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 20 μm. The modified polyurethane coating were sprayed on the surface of the carbon steel working electrode to 60 ± 10 μm thick by an air spray method. The coated specimens were then cured in an oven for at 80 °C for 2 h followed by post-curing for 1 day at 25 °C.

2.3. Analysis of surface modification

FT-IR spectroscopy scanning was conducted from 4000 to 650 cm^{-1} of wavelength on the top of the polyurethane coating modified with different contents of HTPS1 and HTPS2. ATR (attenuated total reflection) method was applied at 45° of IR beam. Distribution of the modifier (HTPS) in the modified polyurethane coating was analyzed by measuring the Si peak intensity by ATR mode

Table 1. Composition of polyurethane coat system modified with HTPS1 and HTPS2 at different contents

Modified polyurethane coat system	HTPS1 (wt%)	Modified polyurethane coat system	HTPS2 (wt%)
US1-1	1.0	US2-1	1.0
US1-2	3.0	US2-2	3.0
US1-3	5.0	US2-3	5.0
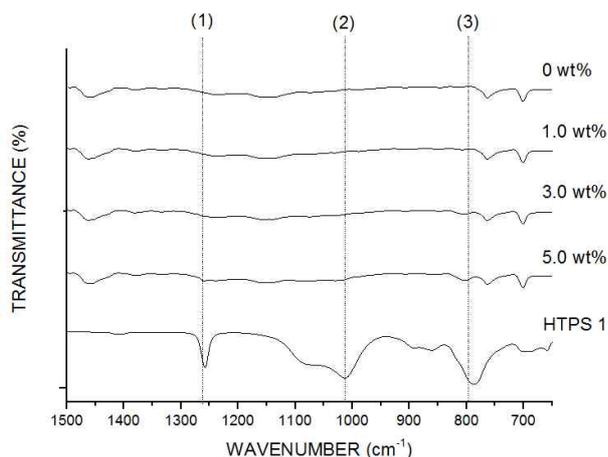
Fig. 3. IR spectra of polyurethane coatings modified with various contents of HTPS1 (Mn: 2,000 g/mol) on the top layer of the coatings.
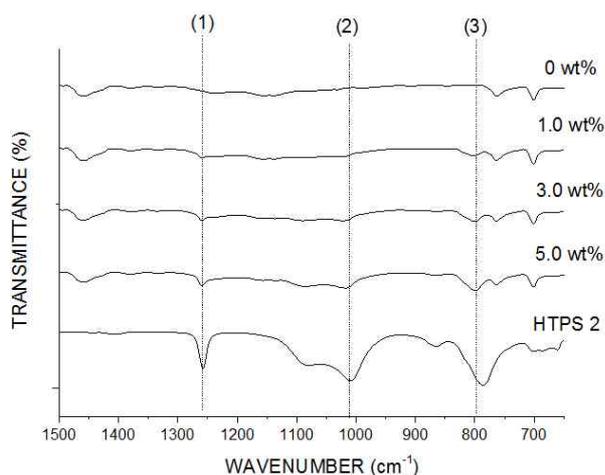
Fig. 4. IR spectra of polyurethane coatings modified with various contents of HTPS2 (Mn: 77,000 g/mol) on the top layer of the coatings.

of FT-IR (Nicolet iS10, USA) since Si element is contained only in HTPS. Fig. 2 shows IR spectrum of pure HTPS in which the peak at 1260 cm^{-1} (1), 1010 cm^{-1} (2), and 790 cm^{-1} (3) are those for CH$_3$ symmetric deformation of Si–CH$_3$, Si–C stretching and rocking, and Si–O–Si stretching vibration, respectively. All of these peaks were used to characterize the existence of HTPS modifier on the surface of coating.

The change in the surface properties of the modified polyurethane system depending on the type and content of the modifier was evaluated by measuring the contact angle using a contact angle meter (Phoenix300, SEO Co. Ltd.) according to the sessile drop method. The contact angle was measured at 10 s after dropping the distilled water on the surface of coated specimens.

2.4. Electrochemical cell and EIS combined with immersion test

Immersion tests were conducted to evaluate the cumulative effects of electrolyte on the coating/metal interface through the diffusion of electrolyte into the coating. Three electrode electrochemical cell consisted with the polyurethane coated carbon steel as a working electrode (exposed area: 6.28 cm^2), a saturated calomel reference electrode, and a platinum counter electrode was used to conduct electrochemical impedance spectroscopy (EIS) test in 0.5M NaCl solution. The impedance and capacitance of the modified polyurethane coated carbon steel electrode was measured by EIS method. The impedance data were obtained by applying a sine wave of 20 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

3.1.1. FT-IR analysis

Fig. 3 shows IR spectra measured on top of the polyurethane coatings modified with HTPS1 as a function of HTPS1 content. From the results of IR spectra, it is observed that the Si–O–Si (1010 cm^{-1}), Si–C (790 cm^{-1}) and Si–CH$_3$ (1260 cm^{-1}) functional group were appeared at HTPS1 content higher than 3 wt% and these peaks were increased with increase of HTPS1 content.

Fig. 4 shows IR spectra measured on top of the polyurethane coatings modified with HTPS2 as a function of HTPS2 content. From the results of IR spectra, it is also observed that the Si–O–Si (1010 cm^{-1}), Si–C (800 cm^{-1}) and Si–CH$_3$ (1260 cm^{-1}) functional group were appeared at HTPS2 content higher than 1 wt% and these peaks were increased with increase of HTPS2 content.

These results clearly demonstrated that the modifier HTPS2 is distributed more in the top of modified polyurethane coatings than HTPS1 modified polyurethane coatings, due primarily to an increase in phase separation tendency between polyurethane and HTPS2 with an increase in the molecular weight of modifier.

3.1.2. Contact angle measurement

A static contact angle was measured on a pure polyurethane coating and also on the polyurethane coatings modified by HTPS1 and HTPS2, respectively, and the results were described in Fig. 5. Evidently, the contact angle was dramatically increased by the addition of modifier with 3 wt% irrespective of the type of modifier. The contact angles on the polyurethane coatings modified with

HTPS2 showed higher than those on the polyurethane coatings modified with HTPS1. These results clearly indicates that the surface of pure polyurethane coating was changed from hydrophilic to hydrophobic due to the modification, and the hydrophobic tendency of the coating surface is more appreciable when the modification was done by a modifier with high molecular weight such as HTPS2.

3.2. Effects of modifier for water transport behaviors

To investigate the diffusion of water through the modified polyurethane 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 equation (1) suggested an empirical expression that relates the capacitance of a coating to the volume fraction of water absorbed into the coating.[7-10]

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

which was expressed by 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 ε_{H2O} 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. (2), called "the initial slope method"[11-12],

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

where, slope is the slope of ln $C_C - t^{1/2}$ plot, and L is thickness of the coating. The capacitance of a coating at the frequency of 1 kHz was selected for the calculation
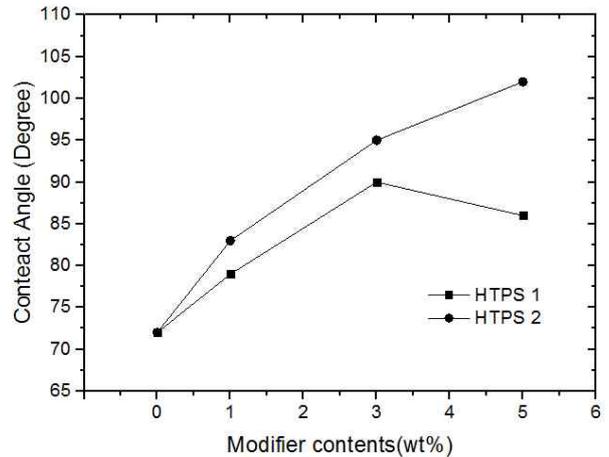

Fig. 5. Effects of modifier content on the contact angle of polyurethane coatings modified with different modifier (HTPS1: Mn: 2,000 g/mol, HTPS2: Mn: 77,000 g/mol) at different contents (0, 1.0, 3.0 and 5.0 wt%).

of diffusion coefficient of water and water uptake (Eq. (1)) through the coating in this work. The ln $C_C - t^{1/2}$ 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.

Table 2 shows diffusion coefficient of water into a polyurethane coating which was calculated from the slope of ln $C_C - t^{1/2}$ curve using Eq. (2), and volume fraction of water uptake which was calculated by Eq. (2). The capacitance of dry coating, C_0, was determined by extrapolation of the ln $C_C - t^{1/2}$ curve at $t = 0$.

Table 2. Volume fraction of water uptake and water diffusion coefficients for modified polyurethane coating systems

Modified coating system	Diffusion coefficient ($\times 10^{-11}$, cm^2/s)	Volume fraction of water uptake (vol%)
Polyurethane	37.3	34.7
US1-1	5.81	2.87
US1-2	6.22	2.81
US1-3	5.01	2.82
US2-1	7.69	3.61
US2-2	5.09	2.81
US2-3	4.58	2.74

The diffusion coefficient of water and the water uptake for the pure polyurethane coating were calculated to be 3.73×10^{-10} m²/s and 34.7 vol % at 25°C, respectively. In the case of modified polyurethane coatings, the calculated diffusion coefficient of water uptake in HTPS1 modified polyurethane coatings was decreased from 5.81×10^{-11} m²/s to 5.01×10^{-11} m²/s with an increase in HTPS1 content to 5 wt%, and the water uptake into the coatings were also decreased from 2.87 vol % to 2.82 vol % at 25 °C with an increase in HTPS1 content. The HTPS2 modified polyurethane coatings shows similar water transport behavior. The calculated diffusion coefficient of water in HTPS2 modified polyurethane coatings was decreased from 7.69×10^{-11} m²/s to 4.58×10^{-11} m²/s with an increase in HTPS2 content to 5wt%, and the water uptake into the coatings were also decreased from 3.61 vol % to 2.74 vol % at 25 °C with an increase in HTPS2 content

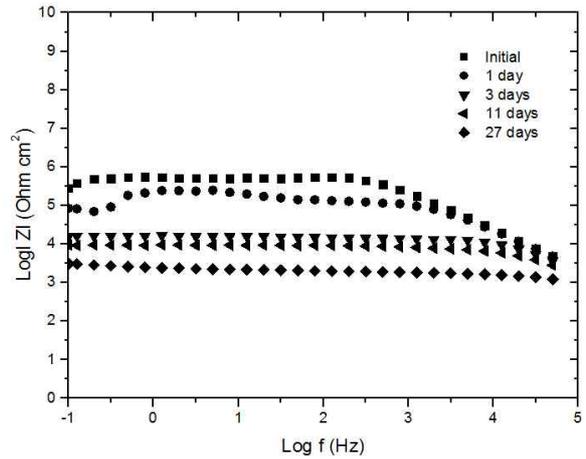These results clearly demonstrate that the water dif-

Fig. 6. EIS spectra in Bode plot for polyurethane coating without modification in immersion test.

fusion coefficients in the polyurethane coatings modified with either HTPS1 or HTPS2 were much lower than that
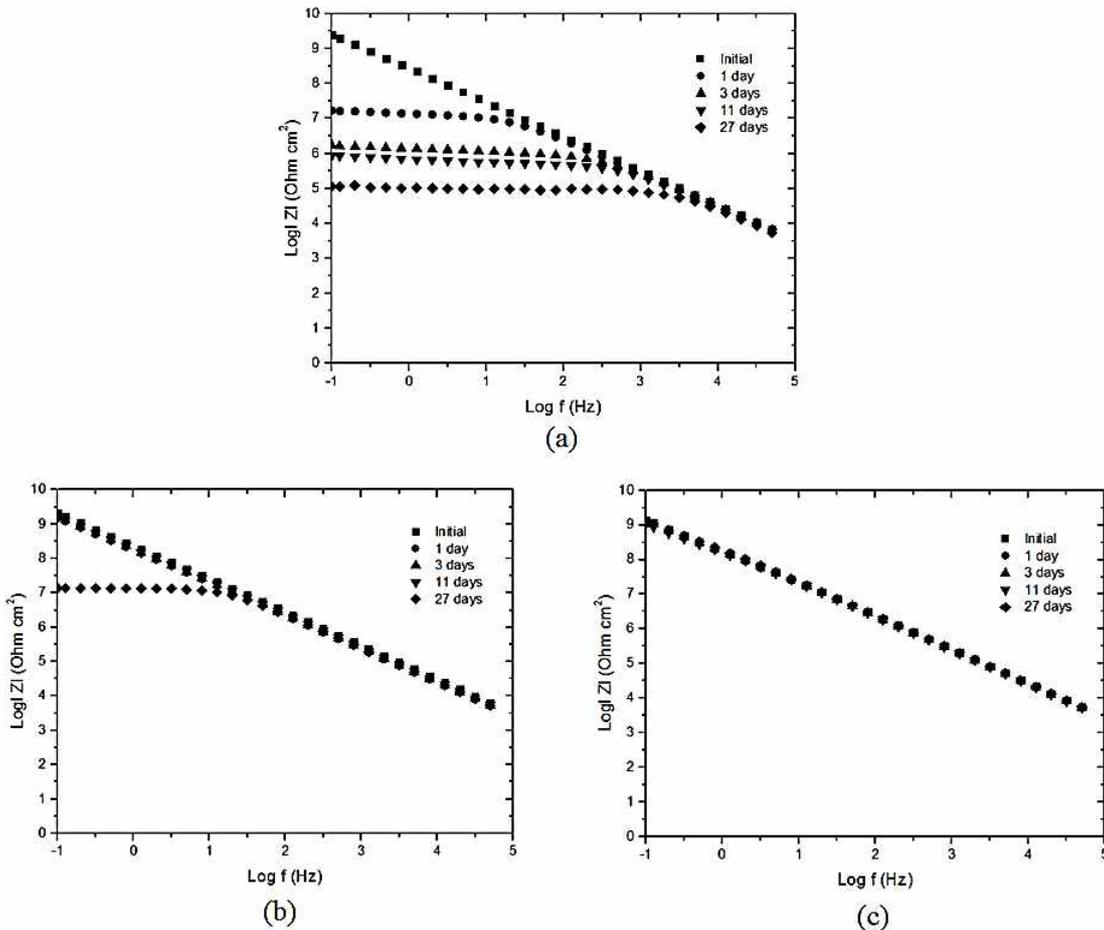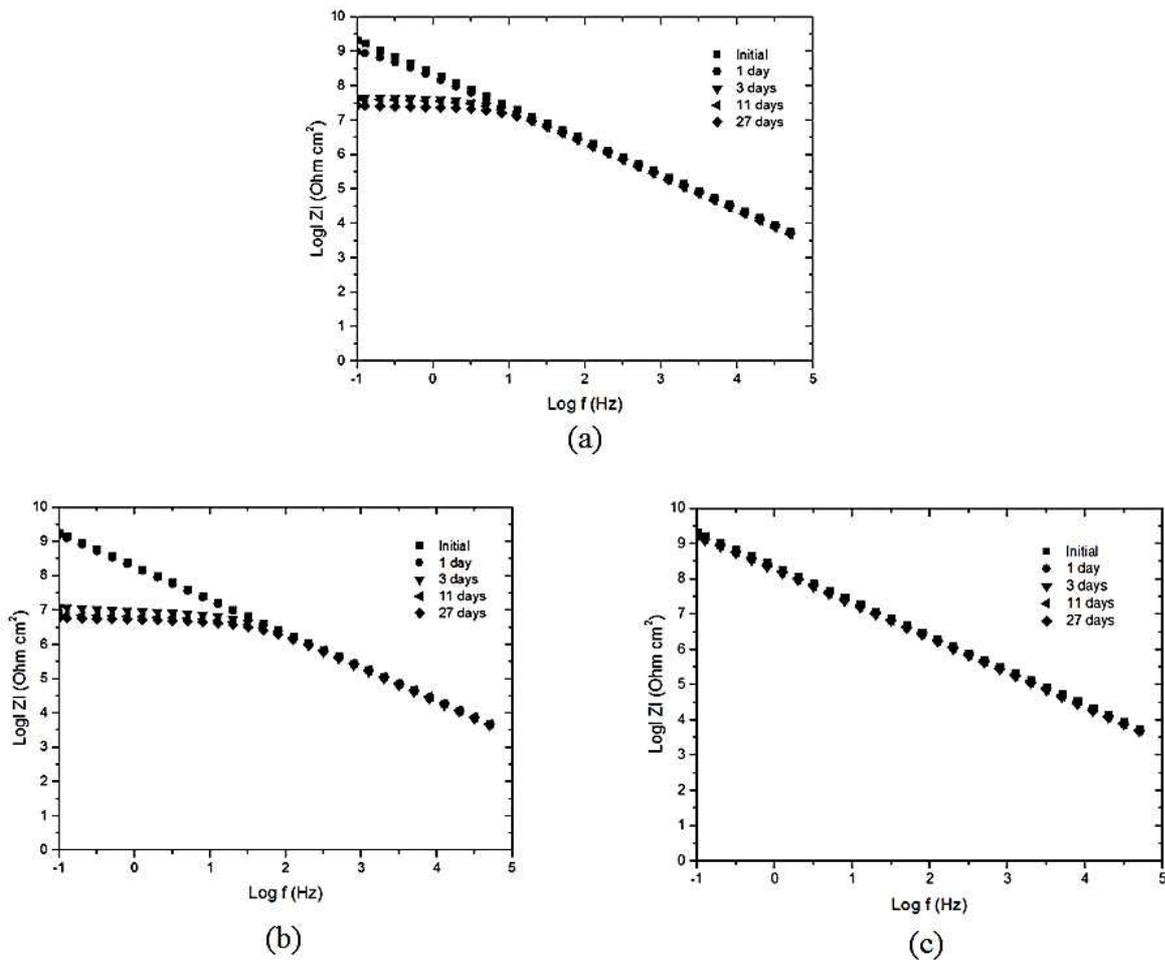

Fig. 7. EIS spectra in Bode plot for polyurethane coating modified with various contents of HTPS1 as a function of immersion time: (a) US1-1, 1.0 wt%; (b) US1-2, 3.0 wt%; and (c) US1-3, 5.0 wt%.

Fig. 8. EIS spectra in Bode plot for polyurethane coating modified with various contents of HTPS2 as a function of immersion time: (a) US2-1, 1.0 wt%; (b) US2-2, 3.0 wt%; and (c) US2-3, 5.0 wt%.

of the pure polyurethane coating, and hence the water up-take into the modified coatings was much less than that into the pure polyurethane coating. However, the decreasing of diffusion coefficients in the modified polyurethane coatings was not significant with increase of modifier contents of HTPS1 and HTPS2

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

The corrosion protection of the modified polyurethane coated steel was examined by EIS combined with immersion test.[13-17] Fig. 6 shows EIS spectrum measured for the unmodified polyurethane coated on steel as a function of time in immersion test. Impedance modulus of log $|Z|$ at 0.1 Hz decreased even after immersion, and then continues to reduce with immersion time to 27 days.

Fig. 7 shows the EIS spectrum as a function of immersion test for carbon steel coated with the polyurethane modified with HTPS1. Evidently, the impedance modulus

$|Z|$ of US1-1 (1 wt% of HTPS1) at 0.1 Hz was dropped to a low value of 1.6 x 10^7 Ω cm^2 after 1 days of immersion and then continues to reduce to 1.1 × 10^5 Ω cm^2 with immersion time to 27 days. On the other hands, the impedance modulus $|Z|$ of US1-2 (3 wt% of HTPS1) was maintained till 11 days of immersion then dropped to a low value of 1.3 × 10^7 Ω cm^2 after 27 days of immersion. However, US1-3 (5.0 wt% of HTPS1) showed the constant impedance modulus at 0.1 Hz even after 27 days of immersion.

Fig. 8 shows the EIS spectrum as a function of immersion time for carbon steel coated with the polyurethane modified with HTPS2. The impedance modulus $|Z|$ of US2-1 (1 wt% of HTPS2) at 0.1 Hz was dropped to a low value of 4.5 × 10^7 Ω cm^2 after 3 days of immersion and then slightly increase to 2.7 × 10^7 Ω cm^2 with immersion time to 27 days. On the other hands, the impedance modulus $|Z|$ of US2-2 (3 wt% of HTPS2) was maintained till 1 days of immersion then dropped to a

Table 3. Impedance values of modified polyurethane coating at 0.1 Hz in terms of immersion time in 0.5M NaCl solution

Specimens	Impedance values in terms of immersion time (log |Z|, Ω cm^2)				
	Initial	1 day	3 days	11 days	27 days
Without modifier	5.5	4.9	4.2	4.0	3.5
US1-1	9.4	7.2	6.2	5.9	5.1
US1-2	9.3	9.2	9.2	9.2	7.1
US1-3	9.1	9.1	9.1	9.0	9.1
US2-1	9.3	9.0	7.0	7.6	7.4
US2-2	9.3	9.2	7.1	6.9	6.8
US2-3	9.3	9.2	9.2	9.2	9.2

low value of 1.2×10^7 Ω cm^2 after 3 days of immersion and then reduce to 6.0×10^6 Ω cm^2 with immersion time to 27 days. However, US2-3 (5.0 wt% of HTPS2) showed the constant impedance modulus at 0.1 Hz even after 27 days of immersion.

When compared the results of water transport behaviors through the modified or the unmodified coatings and impedance analysis, it is evident that the modified polyurethane coating with lower diffusion coefficient or lower water uptake was associated with the less decrease in impedance modulus |Z| at low frequency region with immersion test as listed in Table 3.

4. Conclusions

Conclusions drawn from the study are as follows:
1. The phase separation tendency between polyurethane and HTPS modifier in the modified polyurethane coating is more appreciable in the polyurethane coatings modified with higher molecular weight.
2. The surface properties of pure polyurethane coating was changed from hydrophilic to hydrophobic by the modification, and the hydrophobic tendency of the coating surface is more appreciable when the modification was done by a modifier with high molecular weight.
3. Water diffusivity and water uptake into the polyurethane coatings modified with HTPS were much lower than those into the pure polyurethane coating. However, the effects of modification on the retardation of water transport are more appreciable in the coating modified with higher modifier content.
4. The decrease in the impedance modulus |Z| at low frequency region with immersion test for polyurethane coatings was associated with the change of surface hydrophobic properties of modified polyur-

ethane coatings. The corrosion protectiveness of the modified polyurethane coated carbon steel generally increased either with an increase in the molecular weight of modifier or with an increase in the modifier content, confirming that it is well agree with its water transport behavior.

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