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Corrosion Protection Performance of Polyester-Melamine Coating with Natural Wood Fiber Using EIS Analysis

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In the present study, polyester-melamine coating systems with natural wood fiber (NWF) were prepared and the effects of NWF on the corrosion protectiveness of the polyester-melamine coating were examined using EIS analysis. From the results, higher average surface roughness was observed with increase of NWF content. Water diffusivity and water uptake into the polyester-melamine coatings with NWF were much higher than that into the pure polyester-melamine coating. The decrease in the impedance modulus |Z| was associated with the localized corrosion on carbon steel, confirming that corrosion protection of the polyester-melamine coatings with NWF well agrees with its water transport behavior.

Keywords : *polyester, corrosion protection, EIS, wood fiber, confocal microscopy*

1. Introduction

Organic coatings are widely used to give aesthetic appearance and protection from the destructive environments such as corrosion. 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. Polyester-melamine is thermosetting coating material which is commonly used in pre-coated metal (PCM) industry such as roofing, building exterior and household electrical appliance[1-2]. It is cured in gas convection oven at a peak metal temperature (PMT) of 216 ~ 270 ℃. Generally, coating applies to both interior and exterior area and the corrosion protection performance of coating is determined by their barrier properties and adhesion performance between coating and substrate. Basically, there are two typical corrosion protection mechanisms of coatings. Therefore, fillers or pigments are very important component to give barrier properties and adhesion strength for coating systems.

NWF consists of cellulose, hemicellulose and lignin, and the dominant component is cellulose[3-5]. NWF is the most important source among the natural fibers. With increase of interest in environmental aspects and natural renewable material, application of NWF in industries has raised and become of importance. NWF is used in paper and paperboard industry over 55 %[6] and fiber reinforced composites[7]. NWF generally showed higher mechanical performance compared with other natural fibers and light weight[8]. Several researchers reported that the addition of NWF increased the modulus and the tensile strength of the composite[9,10].

Heat reflective coatings are very attractive issue for energy saving and several methods are introduced by the addition of mineral insulators in the building industry. Their heat insulation performance has been conducted and confirmed to act as interfering material to heat transmission resulting in reducing heat loss[11]. M. Barletta at al. studied the thermal insulation properties of polyurethane coating with wood fiber and an improved thermal insulation result was achieved[12].

As discussed above, NWF is very useful materials in various application fields however, the introduction and application of NWF as a filler in organic coating, especially, corrosion protection performance, was rarely reported.

The objective of present work is to develop a polyester-melamine coat system by adding the NWF and then to examine the effects of the wood fiber on the corrosion protectiveness of the polyester-melamine coating using electrochemical impedance spectroscopy analysis.

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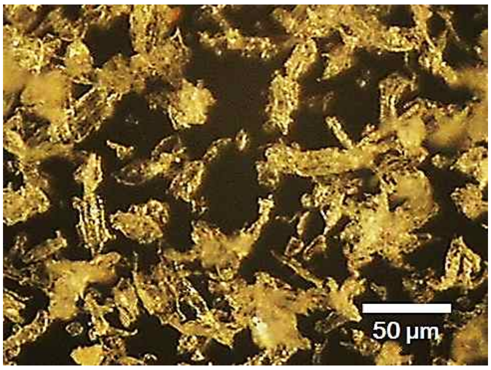

Fig. 1. Optical microscopic images of natural wood fiber.

2. Experimental

2.1. Materials

Polyester-melamine (supplied by PPG, Korea) was used for present coating system and NWF with average 5 μm length (supplied by G-biotech, Korea) used as a reinforcement. Isopropyl alcohol was used as solvent of coating with 20 wt%. The NWF was observed by optical microscope as shown in Fig. 1.

2.2. Preparation of coating specimens

NWF added polyester-melamine coatings were prepared by mixing with polyester-melamine resin, solvent and NWF according to the designed ratio as specified in Table 1. The mixtures were vigorously stirred and degassed for 10 min using ultrasonic bath. Before coating, the surface of the cold rolled carbon steel sheets (KS D3512 SCP1-S, supplied by POSCO, Korea) was pretreated by abrasive paper (# 200), 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 about 2 ~ 3 μm. The NWF added polyester-melamine coatings were coated on carbon steel (150 mm × 75 mm × 3 mm) with 20 ± 5 μm thick by bar coating method, and then cured at 270 °C for 2 min.

2.3. Analysis of coating

In order to confirm the chemical structure of NWF and polyester-melamine coating, FT-IR spectroscopy analysis was conducted from 4000 to 650 cm^{-1} of wavelength. ATR (attenuated total reflection) method was applied at 45° of IR beam. 3-D laser confocal microscope (Carl Zeiss LSM 700, Germany) was used to observe the change of morphology on the surface of polyester-melamine coating in terms of NWF contents. In order to find the distribution of NWF in polyester-melamine coatings, the cross-sections of coating were observed by SEM.

Table 1. Composition of polyester-melamine coat system at different NWF contents

NWF reinforced polyester-melamine coat system	NWF contents (wt%)
NPM-1	0
NPM-2	5.0
NPM-3	10.0
NPM-4	20.0

2.4. Water transport behaviors into the coating

To evaluate the diffusion behaviors of water through the NWF added polyester-melamine 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[13-16].

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

Where V_t is volume fraction of absorbed water at time t, C_0, C_t are the capacitances of 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). In addition, the diffusion coefficient of water into an organic coating was calculated by Eq. (2), called ''the initial slope method''[17,18],

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

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 of diffusion coefficient of water and water uptake (Eq. (1)) through the coating in present work.

2.5. 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[19]. Three electrode electrochemical cell was used to conduct electrochemical impedance spectroscopy (EIS) test in 0.35

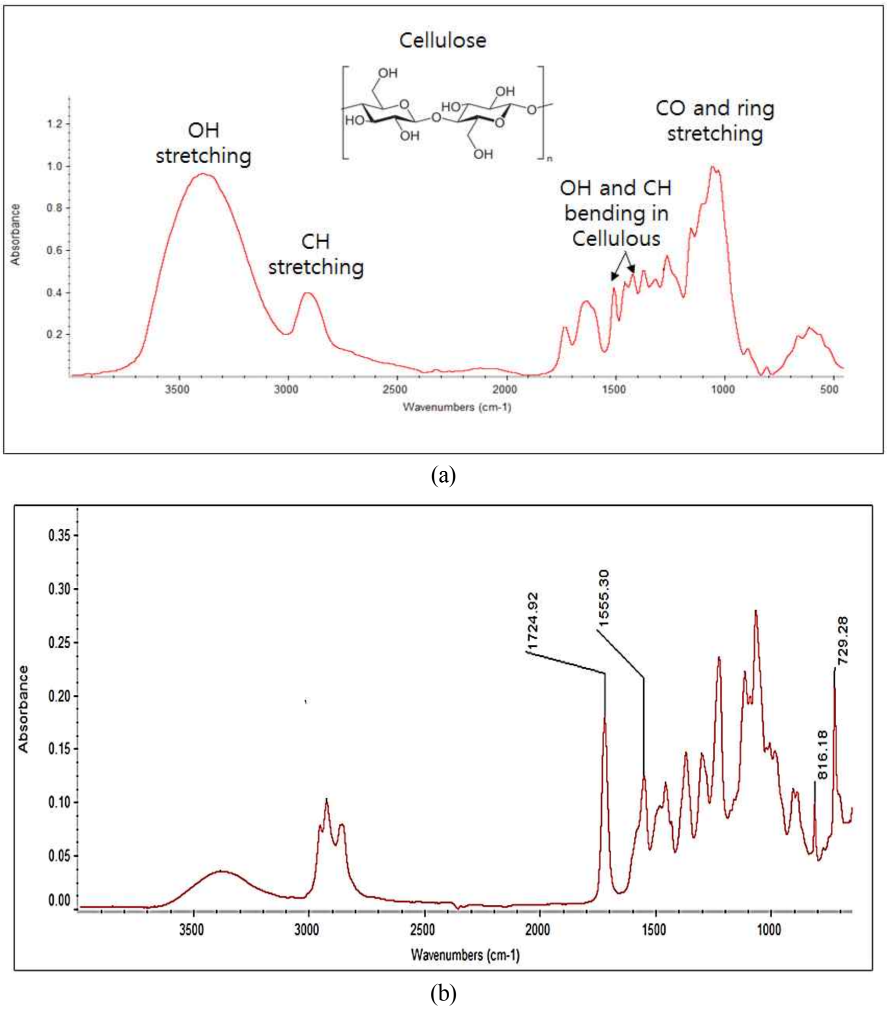

Fig. 2. FT-IR spectrum of natural wood fiber (a) and polyester melamine resin (b).

wt % NaCl solution at 40 °C in which there are NWF added polyester-melamine coated carbon steel as a working electrode (exposed area: 6.28 cm^2), a saturated calomel reference electrode, and a platinum counter electrode. The coating resistance (R_c), coating capacitance (C_c), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of the NWF added polyester-melamine coated carbon steel electrode was measured by EIS in terms of immersion time and corrosion process of NWF added polyester-melamine coated carbon steel was analyzed using equivalent circuit. The impedance data were obtained by applying a sine wave of 20 mV amplitude as a function of frequency ranged from 100 kHz to 10 mHz.

3. Results and Discussion

3.1. FT-IR analysis and surface morphology of NWF

Chemical structure of NWF was analyzed by FT-IR ATR mode as shown in Fig. 2 (a). Analyzed IR spectrum was confirmed as cellulose structure by observation of C-OH bending of 1455 cm^{-1} and CH bending of 1420 and 1365 cm^{-1}. Additionally, hydrophilic OH groups were observed at 3330 cm^{-1}, therefore, water affinity of NWF was considered as very high. In addition, the chemical structure of polyester-melamine coating was also analyzed by FT-IR ATR mode as shown in Fig. 2 (b). In-plane deformation and out-of-plane deformation of triazine ring in melamine were observed at 1545 cm^{-1} and 815 cm^{-1}, respectively, and C=O stretching and out-of-plane bending mode of the aromatic C-H group in polyester were observed at 1725 cm^{-1} and 725 cm^{-1} , respectively.

Fig. 3 shows the cross section images of polyester-melamine coatings with different contents of NWF by SEM. From the results, fairly uniform distribution of NWF in coating was observed and these were arranged by parallel to the carbon steel. In order to evaluate the

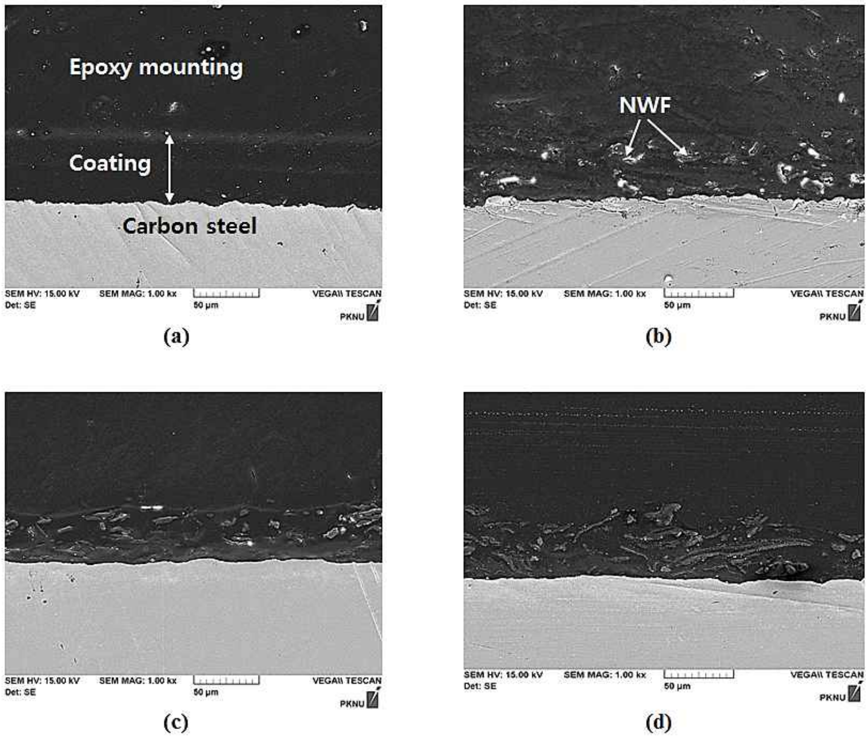

Fig. 3. SEM images for cross section of polyester-melamine coatings with different contents of natural wood fiber: (a) without NWF, (b) 5 wt% of NWF, (c) 10 wt% of NWF and (d) 20 wt% of NWF.

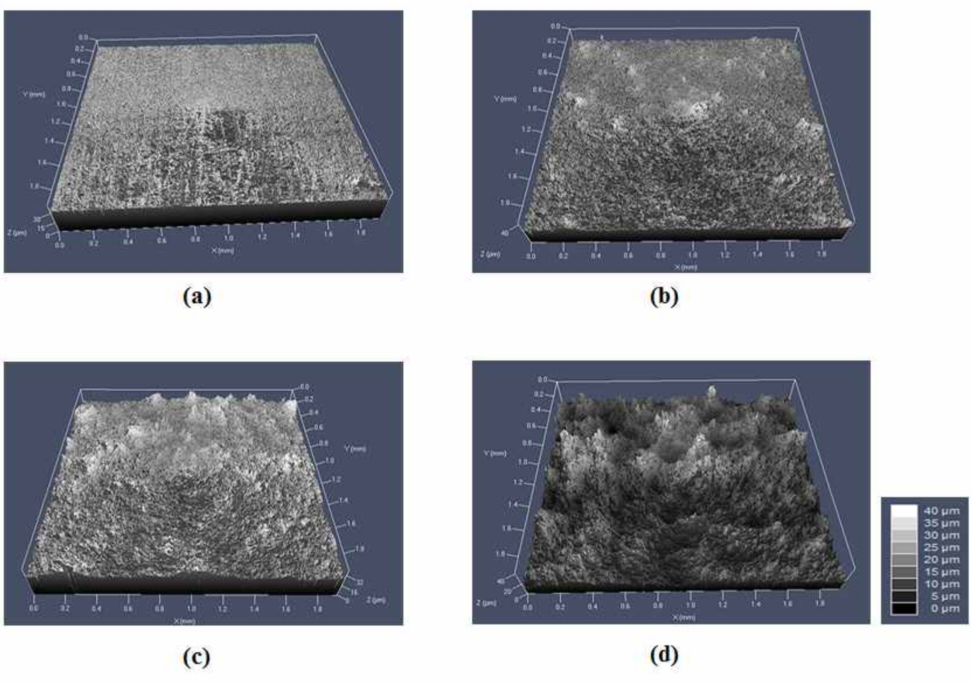

Fig. 4. Surface morphology changes of polyester-melamine coatings with different contents of natural wood fiber by 3-D laser confocal microscope : (a) without NWF, (b) 5 wt% of NWF, (c) 10 wt% of NWF and (d) 20 wt% of NWF.

effects of NWF contents on the surface morphology changes of polyester-melamine coatings, coating surfaces were observed by 3-D laser confocal microscope according to the NWF contents. As a result of observation, high-

Table 2. Volume fraction of water uptake and water diffusion coefficients for NWF reinforced polyester-melamine coating systems

Coating system	Diffusion coefficient ($\times 10^{-9}$, cm^2/s)	Volume fraction of water uptake (vol%)
NPM-1	0.013	0.49
NPM-2	0.76	3.11
NPM-3	5.30	6.17
NPM-4	35.61	11.96

er roughness morphology of the coating surfaces was monitored with increase of NWF contents due to protruding of NWF on the surface of coating, as shown in Fig. 4 (b), (c), (d) and (e). The average surface roughness of polyester-melamine coatings was increased from 2.6 μm to 4.2 μm with an increase of NWF content from 5 wt% to 20 wt%, respectively. On the other hands, almost flat surface morphology was observed in the case of coating without NWF and average surface roughness was 1.7 μm, as shown in Fig. 4 (a). Accordingly, it was indicated that the surface appearance of polyester-melamine coatings was affected by NWF contents.

3.2. Effects of NWF on water transport behaviors into the coating

The ln $C_C - t^{1/2}$ curve of an organic coating generally 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.

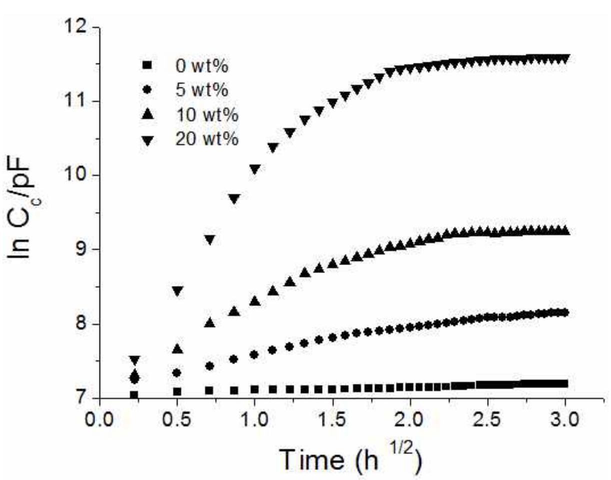

Fig. 5. ln $C_C - t^{1/2}$ curve for polyester-melamine coatings with different contents of natural wood fiber, measured in 0.5 wt% NaCl solution.

Table 2 and Fig. 5 shows the diffusion coefficient of water into polyester-melamine coatings with different contents of NWF 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. (1). The capacitance of dry coating, C_0, was determined by extrapolation of the ln $C_C - t^{1/2}$ curve at $t = 0$.

The diffusion coefficient of water and the water uptake for the pure polyester-melamine coating were calculated as 0.013×10^{-9} cm^2/s and 0.49 vol% at 25 °C, respectively. In the case of polyester-melamine coating with NWF, the calculated diffusion coefficient of water in polyester-melamine coating was increased from 0.76×10^{-9} cm^2/s to 35.61×10^{-9} cm^2/s with an increase in NWF content from 5 wt% to 20 wt%, and the water uptake into the coatings was also increased from 3.11 vol% to 11.96 vol% with an increase in NWF content from 5 wt% to 20 wt%. These results clearly demonstrate that the water diffusion coefficients in the polyester-melamine coat with NWF were much higher than that of the pure polyester-melamine coating, and hence the water uptake into the polyester-melamine coating with NWF was also much higher than that into the pure polyester-melamine coating. From the results, NWF in polyester-melamine coating acts as water absorption promoter rather than barrier protection filler and it may be caused by hydrophilic properties of NWF.

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

The corrosion protection of the NWF added polyester-melamine coated carbon steel was examined by EIS combined with immersion test[12-16]. Fig. 6 (a) shows EIS spectrum measured by the pure polyester-melamine coated carbon steel as a function of time in immersion test. Impedance modulus of |Z| at 0.1 Hz was 1.4×10^8 Ω cm^2 after 3 h. immersion, and then continually reduces

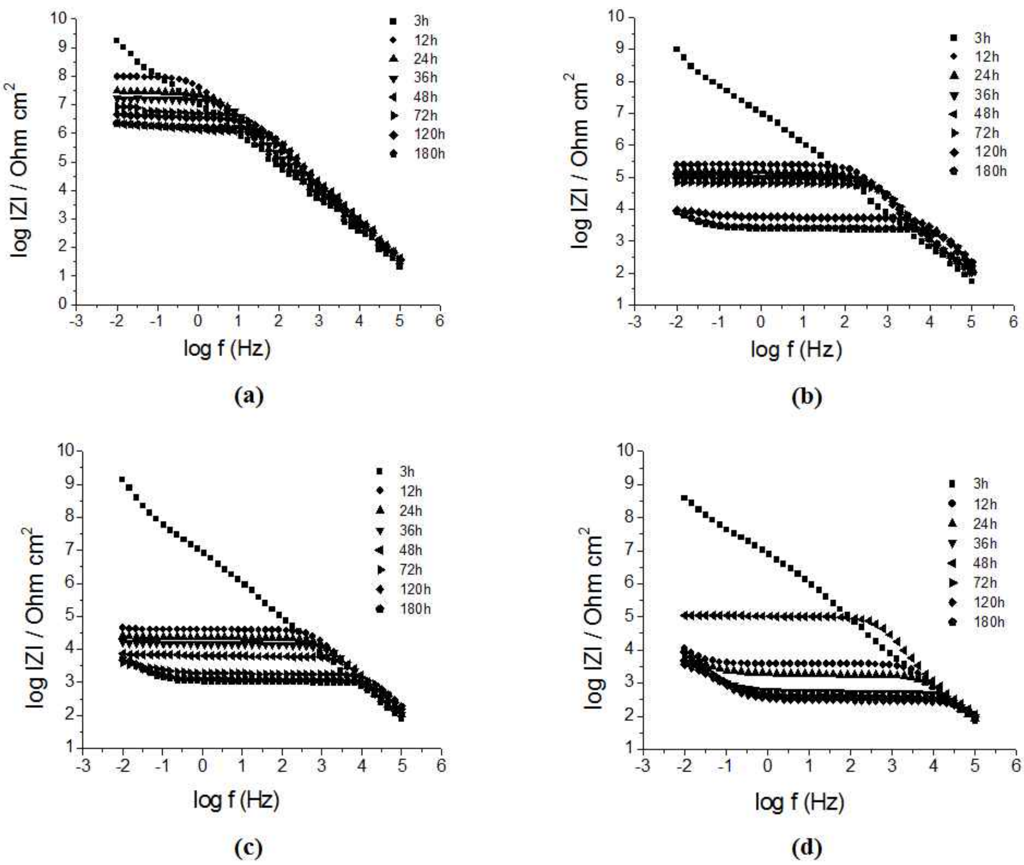

Fig. 6. EIS spectra in Bode plot for polyester-melamine coatings with various contents of natural wood fiber as a function of immersion time: (a) pure (b) 5 wt% of NWF; (c) 10 wt% of NWF; and (d) 20 wt%. of NWF.

to 1.9 × 10^6 Ω cm^2 with immersion time to 180 h. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were not observed during the immersion time to 180 h. From the results, it was clearly indicated that water was permeated into the coating during the immersion time and it lead decrease of coating resistance (R_c) and increase of coating capacitance (C_c) resulting in decrease of impedance, however, delamination phenomenon not occurred at interface between coating and carbon steel.

Fig. 6 (b) shows the EIS spectrum of carbon steel coated with the polyester-melamine with 5 wt% of NWF as a function of immersion time. Evidently, the impedance modulus |Z| at 0.1 Hz was sharply dropped to a low value of 2.5 × 10^5 Ω cm^2 after 12 h. of immersion and then continues to reduce to 6.7 × 10^4 Ω cm^2 with immersion time to 72 h. without enhancement of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). After that, impedance modulus |Z| at 0.1 Hz was dramatically dropped to 6.9 × 10^3 Ω cm^2 after 120 h. of immersion with enhancement of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). Therefore, it was clearly demonstrated that decrease of impedance of coating to 72 h. of immersion was caused by permeation of water into the coating without delamination between coating and carbon steel interface, then; delamination occurred after 120 h. of immersion indicated by enhancement of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}).

Fig 6 (c) shows the EIS spectrum of carbon steel coated with the polyester-melamine with 10 wt% of NWF as a function of immersion time. The impedance modulus |Z| at 0.1 Hz was sharply dropped to a low value of 4.0 × 10^4 Ω cm^2 after 12 h. of immersion and then continues to reduce to 1.5× 10^4 Ω cm^2 with immersion time to 36 h. without charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). Then, impedance modulus |Z| at 0.1 Hz was dramatically dropped to 2.7 × 10^3 Ω cm^2 after 72 h. of immersion with enhancement of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). All measured impedance modulus |Z| at 0.1 Hz with immersion time was lower than those of polyester-melamine with 5 wt% of NWF. The delamination between coating and car-

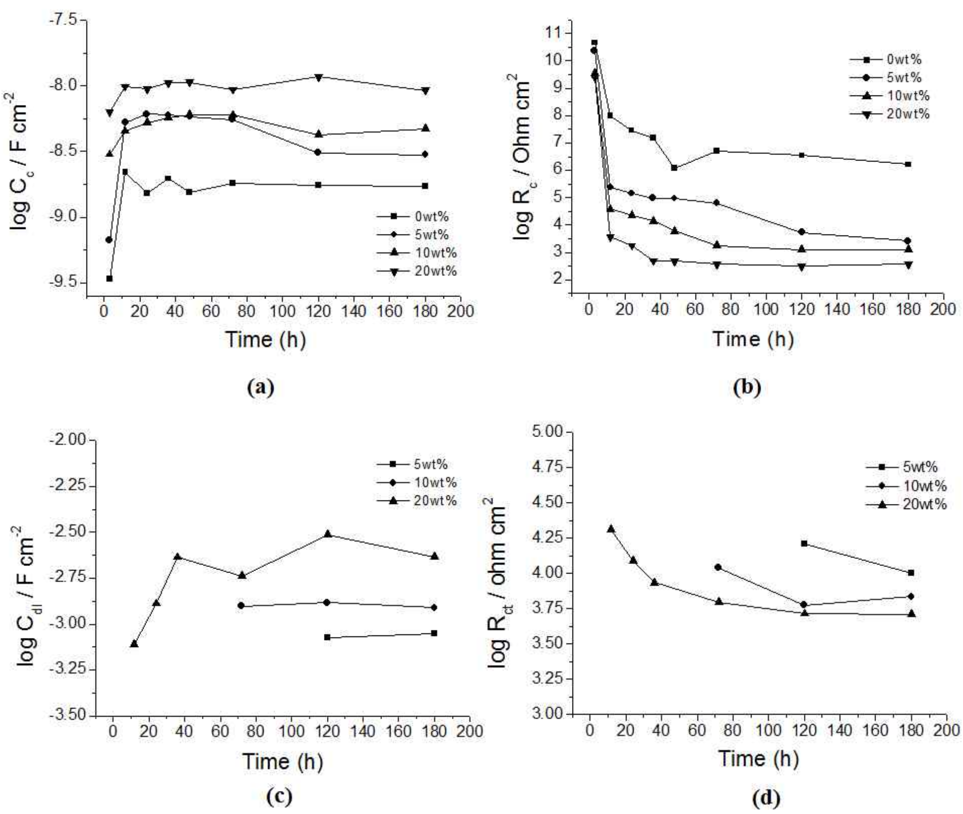

Fig. 7. The changes of C_c *(a)*, R_c *(b)*, C_{dl} *(c) and* R_{ct} *(d)* of polyester-melamine with various contents of natural wood fiber in terms of immersion time.

bon steel interface occurred after 72 h. of immersion which was earlier than polyester-melamine with 5 wt% of NWF.

Fig. 6 (d) shows the EIS spectrum as a function of immersion test for carbon steel coated with the polyester-melamine with 20 wt% of NWF. The impedance modulus |Z| at 0.1 Hz was sharply dropped to a low value of 4.2×10^3 Ω cm^2 after 12 h. of immersion with enhancement of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). Then, impedance modulus |Z| at 0.1 Hz was dropped to 1.2×10^3 Ω cm^2 after 180 h. of immersion. All measured impedance modulus |Z| at 0.1 Hz was lower than those of polyester-melamine with 5 wt% and 10 wt% of NWF. From the results, delamination between coating and carbon steel interface was occurred after 12 h. of immersion with considering of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) enhancement. Accordingly, it was clearly explained that the permeation rate of water into the polyester-melamine coating is more appreciable to the coating with higher contents of NWF and it strongly affect the coating failure on carbon steel resulting in corrosion reaction of carbon steel.

The changes of R_c, C_c, R_{ct} and C_{dl} of polyester-melamine with various contents of NWF were achieved by fitting of Nyquist plot using EC-LAB software and described in Fig. 7 in terms of immersion time. The coating capacitance (C_c) was increased dramatically in initial immersion stage and maintained the constant values. Relatively higher coating capacitance values observed in higher contents of NWF added polyester-melamine coating system. On the other hands, coating resistance (R_c) was decreased dramatically in initial immersion stage and maintained the constant values. Relatively higher coating resistance values observed in no NWF added polyester-melamine coating system. The double layer capacitance (C_{dl}) of NWF added polyester-melamine coating system was observed according to different immersion time. The double layer capacitance (C_{dl}) of polyester-melamine coating without NWF was not observed, however, 5 wt%, 10 wt% and 20 wt% of NWF added polyester-melamine coating showed double layer capacitance after 120 h., 72 h. and 12 h. of immersion, respectively. On the other hands, charge transfer resistance (R_{ct}) of polyester-melamine coating without NWF was also not observed, however, 5 wt%, 10 wt% and 20 wt% of NWF added polyester-melamine coating showed charge transfer

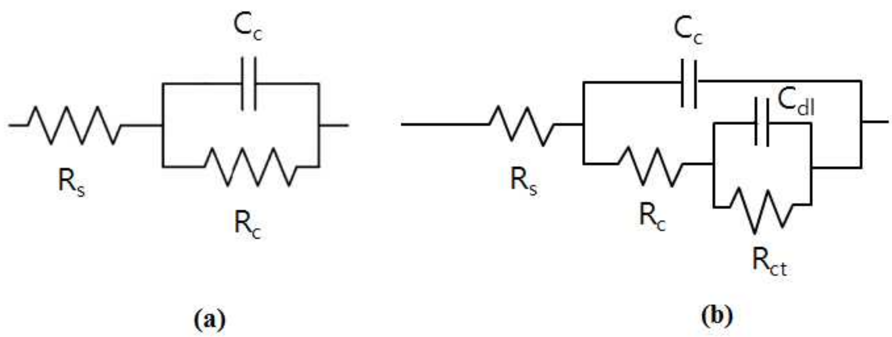

Fig. 8. Establishment of equivalent circuits for (a) pure polyester-melamine and (b) polyester-melamine with natural wood fiber.

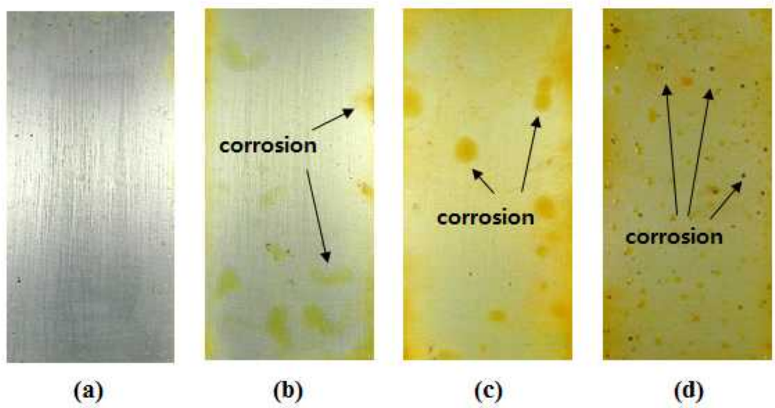

Fig. 9. Corrosion occurrence on the carbon steel coated by polyester-melamine coating after 180 h. of immersion (a) pure polyester-melamine, (b) polyester-melamine with 5 wt% of NWF, (c) polyester-melamine with 10 wt% of NWF and polyester-melamine with 20 wt% of NWF.

resistance after 120 h., 72 h. and 12 h. of immersion, respectively. In present study, equivalent electrical circuit model for coating systems was used, as shown in Fig. 8. It was generally used to describe the water permeation behavior and corrosion reaction of organic coating coated metal[20,21)], where R_s is the electrolyte solution resistance, R_c is the coating resistance, C_c is the coating capacitance, R_{ct} is the charge-transfer resistance and C_{dl} is the double layer capacitance. Using the above parameters, satisfactory fittings were achieved to the experimental EIS spectrum and finally, the electrical circuits can be established as in Fig. 8 (a) and (b) for pure polyester-melamine and NWF added polyester-melamine coating system, respectively.

Fig. 9 shows the corrosion occurrence of polyester-melamine coated carbon steel surface in terms of NWF addition. 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 immersion test. For the carbon steel coated with the polyester-melamine without NWF, corrosion phenomenon was not observed. On the other hands, size of corrosion spots appears coarser and higher occurrence density with increase of NWF contents in polyester-melamine coating. When compared the results in water transport behaviors through the coatings with and without NWF, it is evident that the modified polyester-melamine coating with lower diffusion coefficient or lower water uptake caused less corrosion attack on carbon steel. Further, the decrease in the impedance modulus |Z| at low frequency region with immersion test for the pure or NWF added polyester-melamine coatings 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 study are as follows:

1. NWF was distributed in polyester-melamine coatings uniformly and arranged by parallel to the carbon steel. Higher average surface roughness was observed with increase of NWF contents. Therefore, it was indicated that

the surface appearance of polyester-melamine coatings was affected by NWF contents.

2. Water diffusivity and water uptake into the polyester-melamine coatings with NWF were much higher than those into the pure polyester-melamine coating. The effects of NWF on the acceleration of water transport behaviors into polyester-melamine coating are more appreciable with higher contents of NWF.

3. The decrease in the impedance modulus |Z| at low frequency region with immersion test in 3.5 wt% NaCl solutions for polyester-melamine coatings was associated with the localized corrosion on carbon steel. The size of corrosion spot and its occurrence density of the polyester-melamine coatings with NWF generally increased with an increase in NWF content,

confirming that corrosion protection of the polyester-melamine coatings with NWF is well agree with its water transport behavior.

Acknowledgement

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