A Study on Kaolin and Titanium dioxide affecting Physical Properties of Electrocoating

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The electrocoating for automotive bodies is pigmented with a mixture of titanium dioxide and kaolin. In this study, the effects of titanium dioxide and kaolin contents in coating on electrodeposition process, drying, and surface properties such as surface roughness, gloss, impact resistance and corrosion resistance were investigated. Titanium dioxide and kaolin in coating do not have a decisive effect on curing reaction during drying and corrosion resistance but on gloss, surface roughness, impact resistance and electrodeposition process of coating. According to its size and shape on coating surface, pigment contents increased during drying process. However, the contents of kaolin and TiO_2 in coating didn't affect the corrosion resistance on zinc phosphated substrate, and the curing properties.

Keywords : *titanium dioxide, kaolin, cataphoretic coating, pigment , extention pigment*

1. Introduction

Pigments have been used to provide chemical and physical properties such as corrosion inhibitor, curing catalyst, coloring, barrier property and filler, and also to enhance coating workability and cost efficiency. Above all, TiO_2 is known for its safe, inexpensive qualities and embodies good optical properties and excellent whitening effect; it dominates majority of white pigment market[1]. It is also frequently used being coated with Al_2O_3, and Mica to maintain stability in waterbone coating. Recently it has been applied as flake form to manifest angle-dependent color or decorative texture[2]. Kaolin is also heavily used as filler in coating industry. It is also known as aluminium silicate ($(OH)_8Si_4Al_4O_{10}$) and composed of 46.54% SiO_2, 39.5% Al_2O_3 and 13.96% H_2O[3,4]. In general, pigment dimensions, sizes and concentration levels affect coating properties such as relative tensile strength, barrier effect and its usage[1,2,5,6]. This study examines painting film resistance during electrodeposition, surface qualities (e.g. surface gloss and roughness) and coating properties (e.g. impact and corrosion resistances) according to relative variations of TiO_2 and kaolin contents. The pigment movement while drying process was also discussed.

2. Experimental Procedures

The formulated electrocoating system in this study was composed of an amine-modified epoxy binder, blocked isocyanate, additives, de-ionized water and pigments. The contents of TiO_2 and kaolin and bath paint were summarized in Table 1 and 2. . A zinc phosphated cold-rolled steel plate was used as a test panel which dimension was 70mm x 150mm x 0.8mm. All of coatings were deposited by electrodeposition building up to 20um-coating thickness and then cured at 170℃ during 20min. in a convection oven. The measurements of surface gloss and roughness averages were made for its surface quality: the gloss of coated surface at 60° was taken by BYK Gardner's gloss detector while surface roughness at 0.8mm cut-off(λ_c) was determined by means of Mitutoyo's LJ201-Roughness Gauge. The changes of functional group were obtained by Fourier transform infrared (FT-IR) analysis. Impact resistance of coating was

Table 1. Pigment contents of coatings

Coating	1	2	3	4	5
TiO2 (%)	11.1%	8.3%	5.5%	2.8%	0.0%
Kaolin (%)	0.0%	2.8%	5.5%	8.3%	11.1%

Table 2. Bath paint conditions for electocoating

	Coating					Remarks
	1	2	3	4	5	
Solid content in bath(%)	19.6	19.7	19.6	19.6	0.2	120℃ × 1hour
ASH in bath (%)	22.7	22.6	22.7	22.5	22.6	630℃ × 1hours
Aging time (hour)	72					at 28℃

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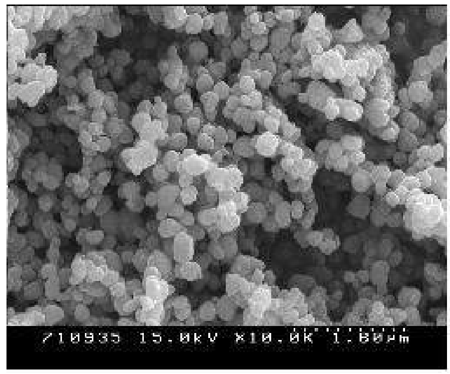
determined by a free-fall-impact tester of Dupont type with 1/2" diameter of rod dropping 1kg weight from 50cm to 20cm. Once dropped, the impacted specimen was immersed in a mixture of 1mole of sulfuric acid solution and 1.2mole copper sulfate for 2 hours in order to determine whether cracks were created or not. Each coated testing panel was manually scribed for salt spray test (SST) and cyclic corrosion test (CCT). SST was performed for 1000hrs and CCT was carried out in the test chamber for 50 cycles: 1 cycle entails SST 4hours at 35℃, drying 2 hours and blister box at 50 ℃-98% R.H. (Nissan Motor's CCT mode 1) And a.c. impedance spectroscopy (EIS) was performed by Solatron's SI Impedance/Gain Phase Analyzer connected to SI 1296 Dielectric Interface on intact coating with $7cm^2$ area in 3.5% NaCl solution at room temperature for 20days.

3. Results and Discussion

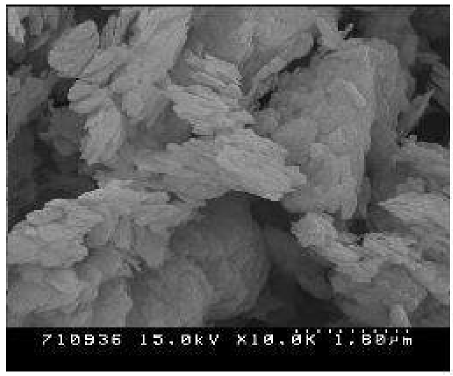
Each TiO_2 and kaolin shape, dimension and content was measured by SEM and EDS. The SEM images are shown in Fig. 1, and compositions of two pigments determined by EDS are presented in Table 3. The differences between two pigments are clearly identified: smaller in size, more regular and spherical shape for titanium dioxide (average dimensions: 0.3um), bigger and irregularly platy shape for kaolin (dimensions: 1um to 10um). In addition, Table 3 shows that TiO_2 was coated with thin film of Al_2O_3.

In order to investigate the effects of TiO_2 and kaolin contents for elecrodeposition process, cataphoretic electrodeposition was carried out at 28℃ for 3min, and electrodeposition voltage and painting resistance at 20um coating thickness were measured accordingly. The results are presented in Table 4: as the content of kaolin was increased, the higher electrodeposition voltage was needed and followed by the increase of painting resistance. It was considered that platy and bigger in size of kaolin might have obstructed a current flow and increased electrodeposition voltage. Although higher electrodepostion voltage gives rise to rupture or gas pinhole defect of coating[7], its defects were not observed in this study. FT-IR analysis was performed to determine the effects of TiO_2 and kaolin contents during curing process. The results are reported in Fig. 2: all spectra present the typical peaks of amine modified epoxy coating.

The peak at $3250cm^{-1}$ indicates C-O-H, and the strong peaks in the region $1050\text{-}1100cm^{-1}$ represent Si-O in kaolin and C-O-C of coating[6]. TiO_2 did not have any effect on such regions: as kaolin content was increased, the peaks at $1050\text{-}1100cm^{-1}$ were increased accordingly while $3300cm^{-1}$ peaks of C-O-H were remained almost same. It can be considered that TiO_2 and kaolin did not directly affect curing reaction in coating process because Si-O peak of kaolin was overlapped with C-O-C peak. The values of gloss and roughness average (Ra) were obtained to evaluate the effects of TiO_2 and kaolin contents on surface quality, and they are reported in Fig. 3 and 4. As increasing TiO_2 content and decreasing kaolin content were, Ra was decreased while gloss was increased. In result, the effects of TiO_2 and kaolin on gloss and roughness are described as follows. The pigment movement in coating during drying process is affected by gravity, viscoelastic force and



(a)



(b)

Fig. 1. SEM image of TiO_2 and kaolin.; (a) TiO_2 , (b) Kaolin.

Table 3. Shape and chemical composition of TiO_2 and kaolin

	TiO_2			Kaolin		
Atomic %	O 78.8	Al 1.5	Ti 19.7	O 73.2	Al 12.5	Si 14.3
Dimension (um)	0.2-0.4			1-10		
Shape	spherical			platy, random		

Table 4. Applied voltage and painting resistance during electrodeposition for 20um coating thickness

	Coating					Remark
	1	2	3	4	5	
Painting voltage at 20um (V)	180	190	210	220	240	3min., 28℃, +/- ratio =1/2
Painting Resistance (㏀-㎠)	822	849	900	906	969	

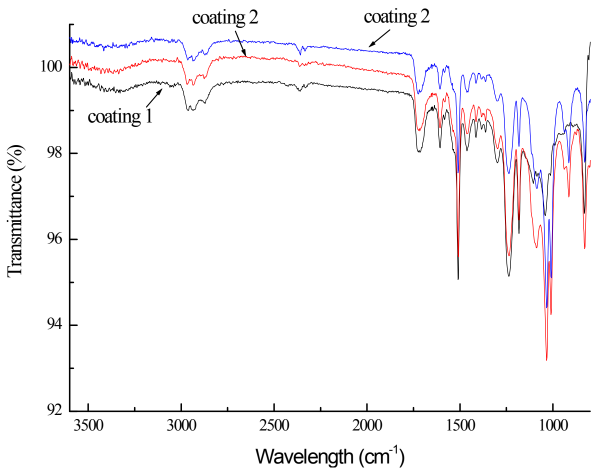


Fig. 2. The result of FT-IR Spectra of coatings.

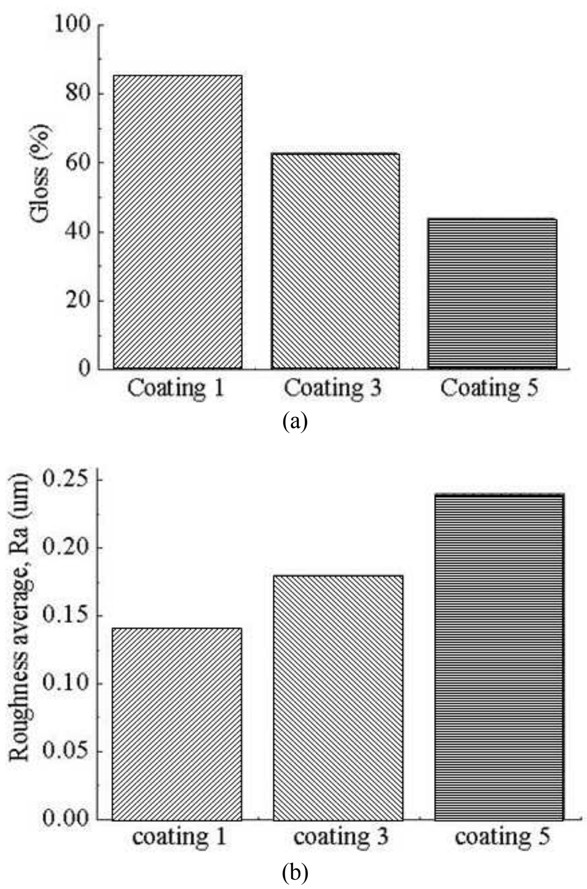


Fig. 3. Results of gloss and surface roughness of coatings (a) gloss (60˚) , (b) Ra (λ_c= 0.8mm x 5).

Table 5. The time dependence of EIS parameters

	Immersion (day)	Cp (F/㎠)	Rp (ohm-㎠)	Cdl (F/㎠)	Rct (ohm-㎠)
Coating 1	1	2.88E-09	9.70E+07	5.60E-10	2.33E+10
	2	2.86E-09	1.43E+07	5.42E-10	2.14E+10
	17	3.00E-09	1.84E+08	1.08E-09	6.11E+09
	18	2.96E-09	1.69E+08	9.45E-10	6.19E+09
	19	2.97E-09	1.78E+08	9.95E-10	6.35E+09
	20	2.96E-09	1.69E+08	9.45E-10	6.19E+09
Coating 3	1	2.89E-09	2.13E+08	8.85E-10	2.11E+10
	2	2.88E-09	6.59E+07	8.79E-10	1.83E+10
	17	2.97E-09	1.08E+08	1.25E-09	1.15E+10
	18	2.96E-09	1.09E+08	1.23E-09	1.26E+10
	19	2.94E-09	1.13E+08	1.18E-09	1.42E+10
	20	2.92E-09	8.02E+07	1.12E-09	1.38E+10
Coating 5	1	2.44E-09	2.62E+07	8.10E-10	1.98E+10
	2	2.48E-09	4.55E+07	9.13E-10	1.36E+10
	17				
	18	2.60E-09	1.15E+08	1.46E-09	8.84E+09
	19	2.94E-09	1.13E+08	1.18E-09	1.42E+10
	20	2.57E-09	1.18E+08	1.44E-09	6.35E+09

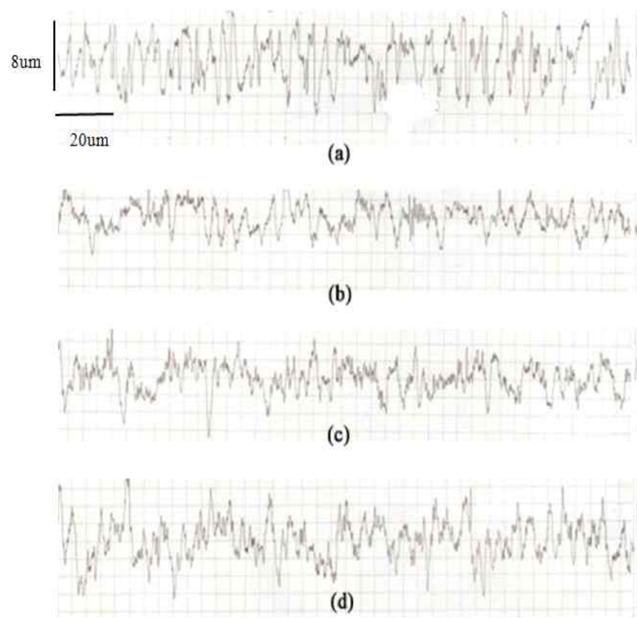


Fig. 4. Surface roughness profile (by λc=0.8mm x 5).of coatings (a) Substrate (Zinc phosphate), (b) Coating 1, (b) Coating 3, (d) Coating5.

surface tension (Fig. 5). Forces associated with increasing viscoelastic properties act on the pigments and tend to oppose the levelling action of surface tension. While curing process is going on, the pigment movement is hindered, continued loss of volume provides rough surface on the coating[8,9]. Because kaolin is bigger in size, platy and irregular in shape than TiO_2 (seen in Fig.1), it is hard to penetrated through in coating. Hence, the pigment increases on coating surface during drying process, and then coated surface becomes rough while the gloss decreases. Free-fall impact test with 1kg-weight was carried out to study the impact resistance of coating with TiO_2 and kaolin contents,

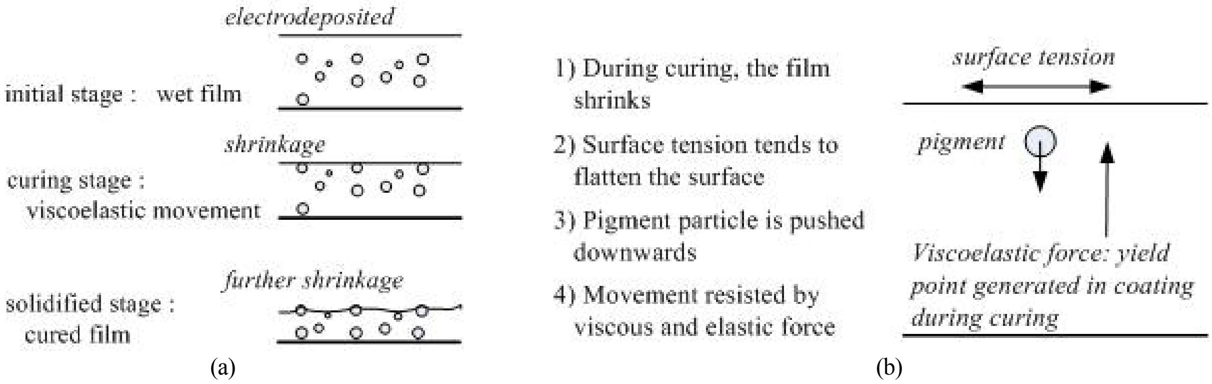
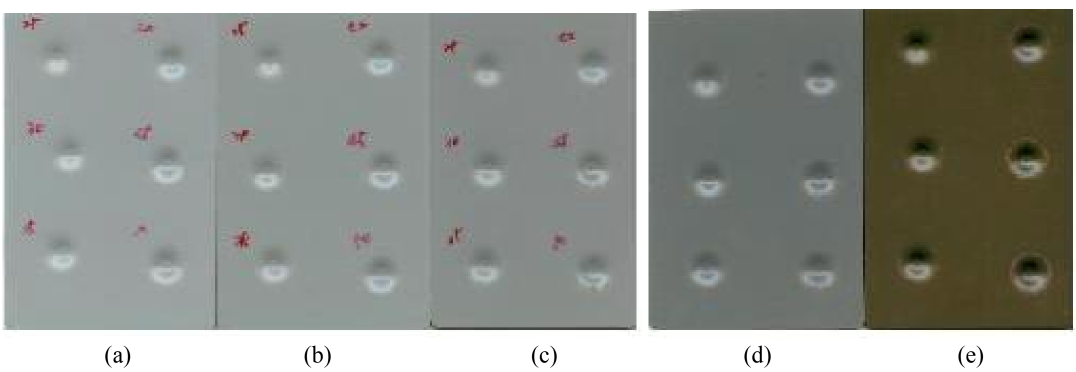


Fig. 5. Schematic diagram to illustrate the formation of cured film[9]. (a) stages during film shrinkage, (b) force at work.



	Coating No.				
	1	2	3	4	5
No crack point(cm)	50	35	25	20	15

Fig. 6. Results of impacted surface of coatings (Impacted face) without crack. (a) Coating 1 at 50cm, (b) Coating 2 at 35cm, (c) Coating 3 at 25cm, (d) Coating 4 at 20cm, (e) Coating 5 at 15cm (Impacted height)

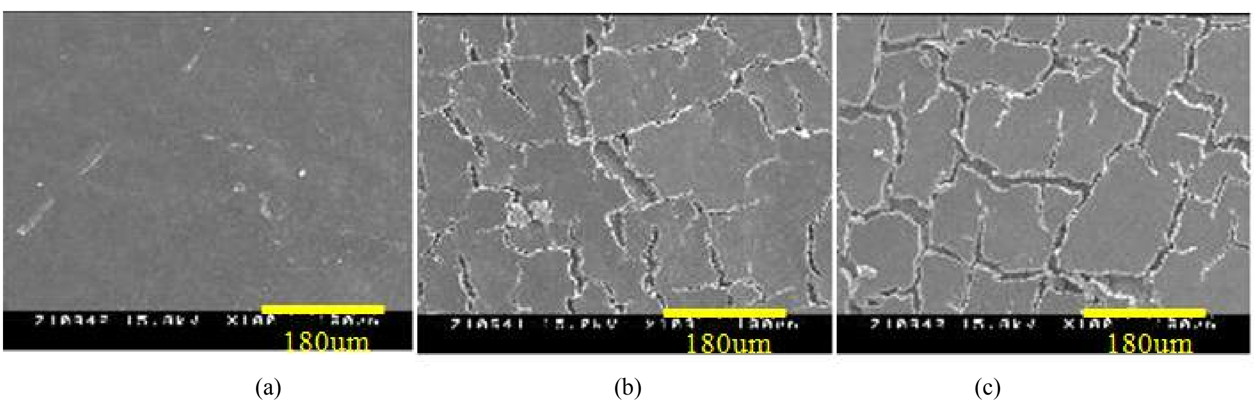
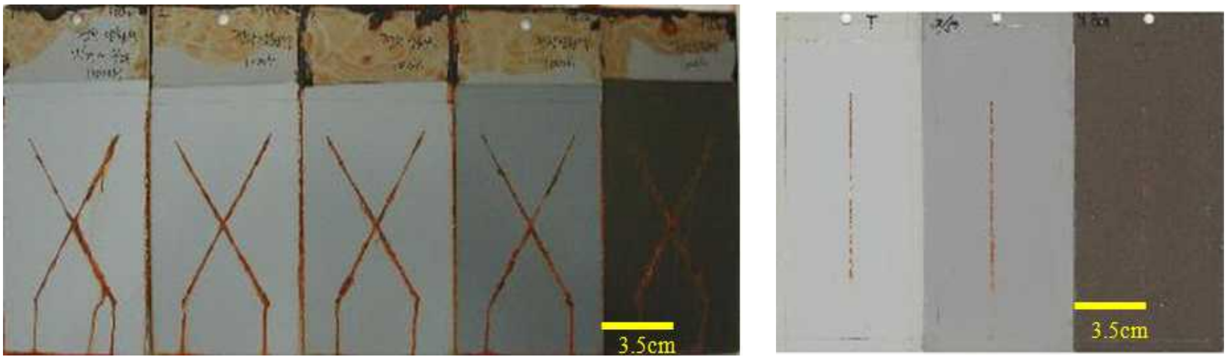


Fig. 7. Results of impacted surface of coatings (The opposite face). (a) Coating 1 at 50cm, (b) Coating 3 at 25cm, (c) Coating 5 at 15cm (Impacted height)

and the results were presented in Fig. 6 and Fig. 7. Fig. 6 shows that no cracks were observed coating 1 which was composed of only TiO_2 while it was impacted by 50cm-height with 1kg weight. Meanwhile, as kaolin content was increased, cracks were observed on coating 5 by 20cm-height impact. Such results demonstrate that impact resistance rises as TiO_2 increases, but opposite results were obtained in the case of kaolin. It seems that the adhesion



(a) (b)

Fig. 8. The result of accelerated exposure tested panels ; (a) The results of 1000 hours exposure tested panels by SST (Coating 1, 2, 3, 4 and 5), (b) The results of 400 hours exposure tested panels by CCT (Coating: 1, 3 and 5).

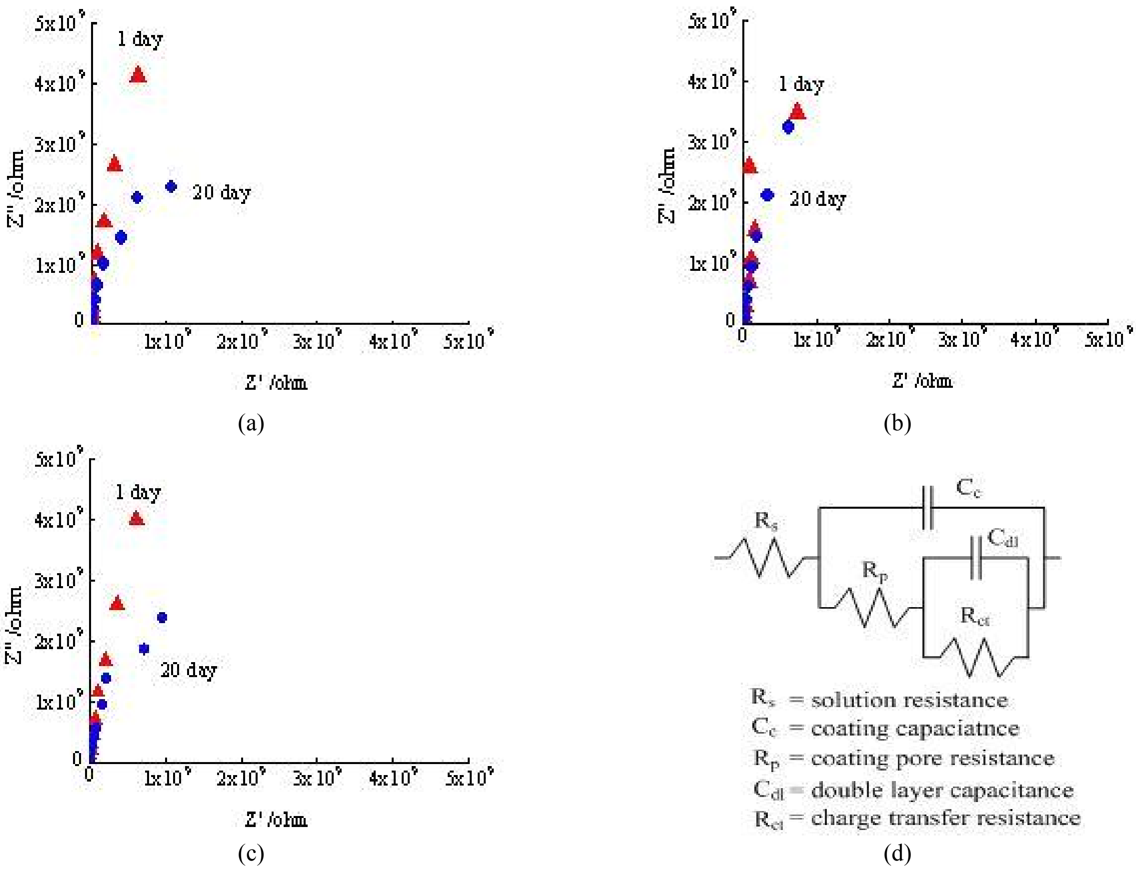


Fig. 9. Impedance spectra for coating 1, 3, 5 and equivalent circuit ; (a) coating 1, (b) coating 3, (c) coating 5, (d) Equivalent circuit for coating.

between platy-type kaolin and resin are weak and these weak interfaces induce initiation of cracks which proceed to propagate rapidly. In order to evaluate corrosion resistance of coating, SST for 1000hour (8a), CCT for 400 hour(8b) and EIS for 20 days were performed by scribed coating. Fig. 8(b) shows the following test results: 1000 hours exposed test panels by SST presented Fig. 8(a), and 400hours exposed test panels by CCT. The results reveal that no de-adhesion or blister on scribed area was not observed. These results represent that relative content variations of kolin and TiO_2 do not affect corrosion resistance on zinc phosphated steels. The results of EIS are shown in Fig. 9 and Table 5. It demonstrates the time dependence of resistances and capacitances which were not dependent on TiO_2 and kaolin contents. In other words, it is considered that there were mere differences among values of

C_c, R_p, C_{dl}, R_{pt} in all specimens, and therefore they were corresponded with the results of SST and CCT.

4. CONCLUSION

Titanium dioxide and kaolin in coating affect notably on gloss, surface roughness and impact resistance. As TiO_2 content increases and kaolin content decreases in coating, the values of gloss and impact resistance were increased while the value of surface roughness was decreased. It is considered that kaolin is difficult to enter in coating because it is relatively bigger in size, platy and irregular shape in comparison with those of TiO_2[4]. The pigment contents increased according to its sizes and shapes on coating surface during drying process. As a result, coating surface had rough and low value of gloss. However, the contents of kaolin and TiO_2 coating didn't affect corrosion resistance on zinc phosphated substrate, and curing process during drying while kaolin did have an effect on electrodeposition process. As the content of kaolin increased, the higher electrodeposition voltage was needed and followed by the increase of painting resistance. It was considered that platy and bigger in size of kaolin in coating would have obstructed a current flow and increased electrodeposition voltage.

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