

# The Failure Behavior of a Polyurethane Composite Coating in 3.5% NaCl Solution under Ultraviolet Irradiation

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**ABSTRACT:** The failure process of inorganic zinc-rich/micaceous iron oxide epoxy/aliphatic polyurethane composite coating in 3.5% NaCl solution under ultraviolet irradiation (UV) was studied with electrochemical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) spectroscopy. UV irradiation significantly accelerated failure process of the composite coating in NaCl solution. The effect of UV on failure process of the coating system in 3.5% NaCl solution may be divided into two stages: in the early stage, the thermal effect generated by the ultraviolet irradiation is the main reason leading to the increase in coating porosity, but this effect is not

serious and the coating remains high impedance and good protection ability. In the latter stage, the fracture of polymer chains in the top coating by UV irradiation is the main factor resulting in quick decrease of coating performance. C—N and C—O bonds in polyurethane coating are broken by UV irradiation, leading to quick increase of the coating porosity and decrease of the coating resistance. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1892–1898, 2011

**Key words:** polyurethane coating; immersion; UV irradiation; failure; EIS

## INTRODUCTION

As a modified polyurethane coating, aliphatic polyurethane coatings show good chemical resistance, weather resistance, and corrosion resistance and have been widely used in various applications.<sup>1</sup> During the performance many environmental factors may lead the coatings to failure, such as: sunlight, pollutants, and temperature, among which ultraviolet ray is a major factor to induce failure.<sup>2</sup> It is very important to understand the influence of UV on aliphatic polyurethane coating and its composite coatings since it is usually used as top coatings.

Electrochemical impedance spectroscopy (EIS) provides rich information about coating properties and failure process which is one of the main technology for coating study.<sup>3–6</sup> Zhang et al.,<sup>7</sup> Zheng et al.,<sup>8</sup> Gonzalez-Garcia et al.,<sup>9</sup> and Armstrong et al.<sup>10</sup> studied the changes of coating porosity, resistance, capacitance, and polarization behavior of acrylic polyurethane coating before and after UV irradiation. Fratricova et al.<sup>11</sup> and Irigoyen et al.<sup>12</sup> studied the aging mechanism of acrylic polyurethane coatings and suggested that the fractured bonds were mainly C—N and C—O bonds during the photo-degradation process of polyurethane coating. Naderi and Mahdavian<sup>13</sup> studied the corrosion and adhesion performance of polyur-

ethane coating on silane pretreated aluminum. Hu et al.<sup>14</sup> studied the aging behavior of acrylic polyurethane varnish coating in two artificial weathering environments. They suggested that the degradation mechanism of acrylic polyurethane in the two weathering environments is basically the same and the degradation occurred under UV conditions is greater than that under Xenotest. However, most of the researches were focused on the aging behavior of acrylic polyurethane coating, the reports on the effect of ultraviolet irradiation plus solution immersion on failure behavior of aliphatic polyurethane coatings are very few. In this article, the failure process of an inorganic zinc/micaceous iron oxide epoxy/aliphatic polyurethane composite coating in 3.5% NaCl solution under UV was studied with EIS, SEM, and Fourier transform infrared (FTIR) to further understand the performance of the composite coating.

## EXPERIMENTAL

### Experimental materials

Paints used in this study were: 8804 inorganic zinc-rich coating as prime, 701-2 micaceous iron oxide epoxy coating as middle coating, and 652 aliphatic polyurethane coating as topcoat which has the chemical structure of —ROOC—NH—R—NH—COO—. The compositions of the coatings were as follows: Inorganic zinc-rich primer: 5% alkyl silicate resin and 75% zinc powers(8–12  $\mu\text{m}$ ); Micaceous iron oxide epoxy coating □43.1% epoxy resin, 6.68% chlorinated

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paraffin, 7.84% iron oxide red, 7.84% zinc oxide, 3.92% mica power, and 3.92% barium sulfate; Aliphatic polyurethane topcoating: 52.7% polyalcohol and 5.3% aliphatic isocyanate resin. All were from Golden Fish Painting Company, Shijiazhuang. The metal substrate was 2 mm thick Q235 carbon steel plate.

### Sample preparation

The steel plates were processed into  $70 \times 40 \text{ mm}^2$  specimens, manually polished with 120# abrasive paper, and cleaned with ethanol and acetone. After drying, the coatings, including inorganic zinc-rich primer (70  $\mu\text{m}$ ), micaceous iron oxide epoxy middle coating (100  $\mu\text{m}$ ), and aliphatic polyurethane top coating (80  $\mu\text{m}$ ), were coated in turn by manual brushing. The intervals between two coatings were 24 h. After the last coating the samples were remained at room temperature for a week to guarantee full solidification before testing.

### Failure testing

The prepared composite coating specimens were divided into two groups. One group was immersed in 3.5% NaCl solution at room temperature, and the other group was immersed in 3.5% NaCl solution under an ultraviolet lamp (365 nm wavelength, 1000 W). The lamp was 50 cm above the solution surface and the specimens were 1 cm under the solution surface. Every 24 h EIS measurements were carried out on the composite coating specimens.

### EIS measurements and FTIR analysis

Electrochemical impedance tests were conducted with a PARSTAT 2273 electrochemical impedance test systems, over the frequency range from 100 kHz to 0.01 Hz at open circuit potential, with a 10 mV potential perturbation. A saturated calomel electrode was as the reference electrode and a platinum film as auxiliary electrode. The testing area was  $12.5 \text{ cm}^2$ .

FTIR analysis was carried out for the polyurethane topcoat after the samples were exposed in 3.5% NaCl solution + UV environment for different times. The FTIR analysis was conducted using a Nicolet 5700 infrared spectrometer (Thermo Electron Corp.), and the window material was KBr.

## RESULTS AND DISCUSSION

### Electrochemical impedance spectra of the composite coatings

Figure 1(a,b) show Bode plots of the polyurethane composite coatings in 3.5% NaCl solution without and with UV irradiation for different times. It is seen that during the initial 10 days of immersion, UV irradiation

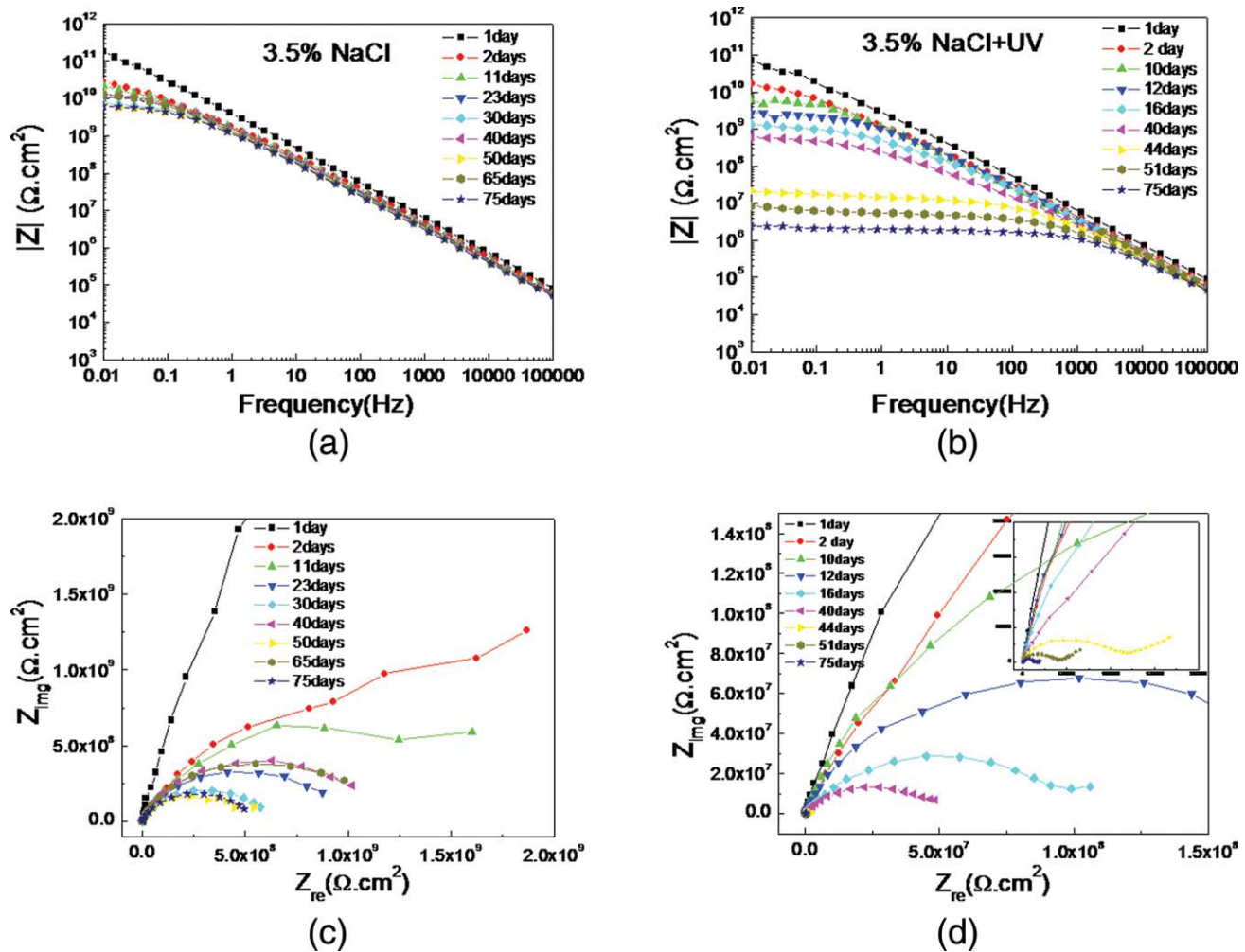
showed no obvious effect on the impedance spectra of the composite coatings. After 10 days, however, UV irradiation significantly accelerated failure process of the coating. After immersion for 75 days, the impedance of the coating sample under UV irradiation at 0.01 Hz decreased below  $10^6 \Omega \text{ cm}^2$  which is a threshold for coating failure.<sup>15</sup> By contrast, the low frequency impedance value of the sample without UV irradiation maintained above  $10^9 \Omega \text{ cm}^2$ , indicating high protection performance. In Nyquist plots [Fig. 1(c,d)], during the early stage there was one time constant for the composite coating systems with or without UV irradiation, indicating that the coatings provide good shield to protect the base metal from corrosion. After immersion for 11 days, a capacitance arc occurs in high-frequency end, and the real part of capacitance arc in low-frequency contracts, which indicates that the electrolytes were penetrating into the pores in the coatings. However, in this stage the substrate corrosion did not happen. For the coating sample without UV irradiation, in Nyquist plot both the capacitance arcs in high-frequency end and in low-frequency range decrease, but until immersion for 75 days no new electrochemical characteristic appears. For the sample with UV irradiation, after 44 days immersion a capacitance arc in high-frequency domain and a diffusion line in low-frequency end are observed in Nyquist plot, which indicates that the composite coating has been penetrated through by electrolytes and the diffusion controlled substrate corrosion has begun. Above characteristics show that ultraviolet irradiation significantly accelerated failure process of the polyurethane composite coatings.

### The coating surface morphology

Figure 2 shows surface morphology of the composite coating after immersion in 3.5% NaCl solution for different times, with or without UV irradiation. The coating surface was observed with a LEO-1450 scanning electronic microscope. For the sample without UV irradiation, the coating surface remained smooth and intact until 75 days. However, under UV irradiation, defects, roughness and peeling off of surface layer were seen on coating surface after only 20 days. With time going on, the coating surface was seriously damaged and peeling off of large areas happened, as shown in Figure 2. It is clear that UV accelerated the formation of pores and the decomposition of the molecular structures.

### Analysis on the impedance parameters

According to Figure 1(b), for the sample without UV, from the beginning until 75 days there was only one capacitance arc in Nyquist plots, indicating that



**Figure 1** EIS spectra of composite coating system under different immersion time. (a) Bode plots in 3.5% NaCl solution and (b) Bode plots in 3.5% NaCl solution + UV. (c) Nyquist plots in 3.5% NaCl solution and (d) Nyquist plots in 3.5% NaCl solution + UV. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

electrolyte has not penetrated to the coating/metal interface and the coating behaved as an effective isolation layer with large resistance and small capacitance. The equivalent circuit in Figure 3(a) may describe the situation. For the sample under UV irradiation, the Nyquist plots showed similar results in the early stage of testing. However, from about 44th day on, the Nyquist plots showed the characteristics of a capacitance arc in high-frequency domain and a diffusion line in low-frequency end, which means that the solution has reached the coating/substrate interface. So the equivalent circuit in Figure 3(b) is suitable to describe this situation,

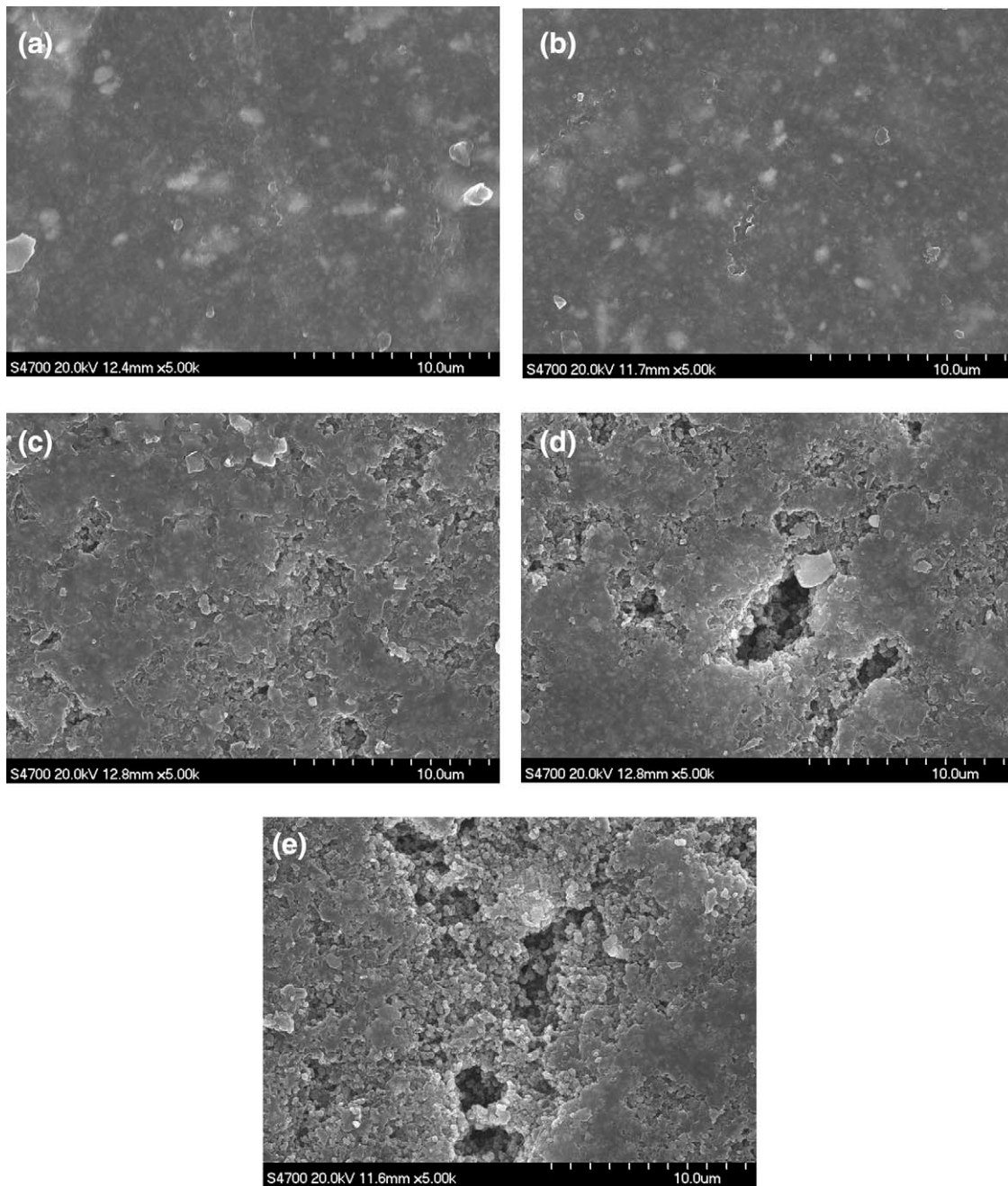
where  $Q$  is coating capacitance,  $R_c$  is coating resistance,  $C_{dl}$  is the double layer capacitance at coating/metal interface,  $R_p$  is the electrochemical reaction resistance at metal interface, and  $L_W$  is the Warburg impedance. Accordance to the equivalent circuits in Figure 3, the impedance spectroscopy data in Figure 1 were analyzed by using software Zsimpwin, and the variations of water uptake  $\phi$  and

coating resistance  $R_c$  with testing time were obtained.

#### Water uptake

It is generally believed<sup>16</sup> that the main effect of coatings is to prevent the infiltration of corrosion mediums. In water environments, water molecules penetrate through the coating by diffusion and result in metal corrosion and the decrease of the binding force between coating and substrate. As the dielectric constant of water (80) is much larger than that of ordinary dry organic coatings (4–5), the coating dielectric constant gets increased after absorbing water and thus the coating capacitance increases. The volume percentage of absorbed water in coating (Fig. 4) may be estimated according to Brasher and Kingsbury equation:

$$\phi = \frac{\log(C_t/C_0)}{\log 80}$$



**Figure 2** SEM morphology map of composite coatings under different immersion time. (a) 0 day, (b) 75 days (3.5% NaCl), (c) 20 days (3.5% NaCl+UV), (d) 40 days (3.5% NaCl+UV), and (e) 75 days (3.5%NaCl+UV).

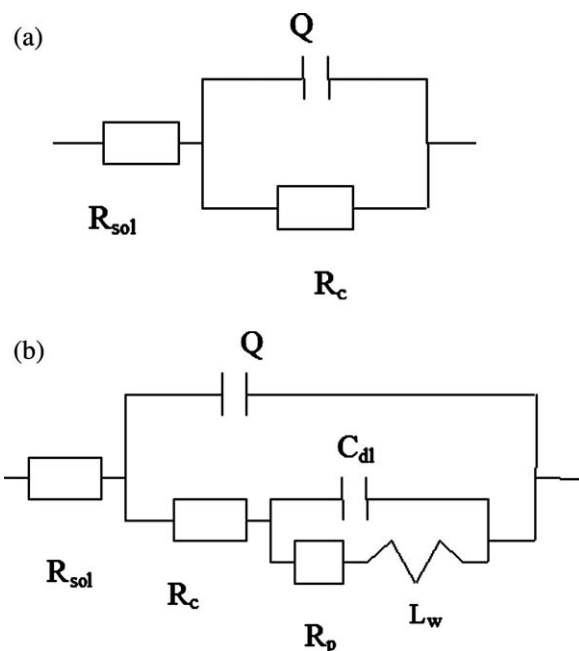
where  $\Phi$  is volume percentage of water absorption, 80 is the dielectric constant of water at 25°C,  $C_0$  is the coating capacitance before immersion, and  $C_t$  is the coating capacitance after immersion time  $t$ .

It is seen from Figure 4 that water absorption of coating shows a two-stage increase in 3.5% NaCl solution under UV. At the beginning water absorption increased rapidly and soon reached the absorption saturation. This period is the slow diffusion process of ions in the coating. After certain time, water absorption of the coating increased rapidly again. During the whole process, water absorption of the coatings grew

continuously. After 75 days immersion the water absorption was up to 60%. While at the same time, water absorption remained unchanged in 3.5% NaCl solution, around 10%.

#### Coating resistance

It is seen from Figure 5 that in 3.5% NaCl solution both with and without UV, the resistances of the composite coatings decreased quickly in the initial two days, which may be attributed to the quick permeation of water into the coatings. However,

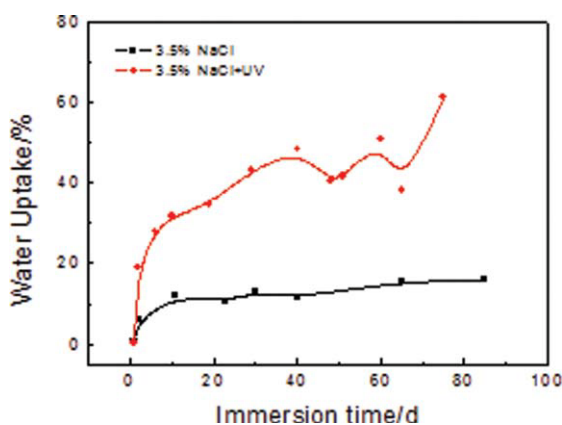


**Figure 3** Equivalent circuit of composite coating/metal system.

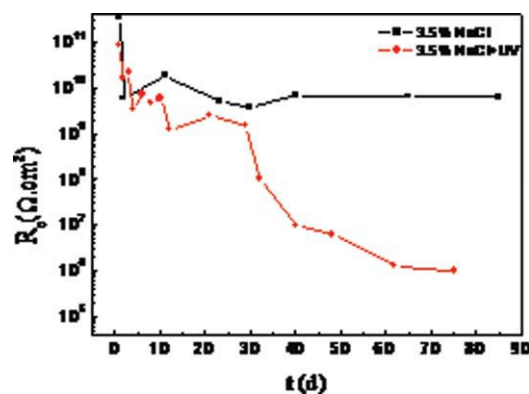
after the initial two days until the 29th day the coating resistances for both situation remained stable values between  $10^9 \sim 10^{10} \Omega \text{ cm}^2$ . The coating resistance under UV showed only a slight decrease than that without UV. Under UV irradiation the solution temperature would increase to some extent, inducing evaporation of residual solvents in coatings, which may result in increased porosity and decreased surface roughness in coatings.<sup>17</sup>

### FTIR analysis

However, for the samples under UV irradiation, the coating resistance decreased significantly from the 29th day on. This phenomenon should be due to



**Figure 4** Water uptake of composite coating changes with time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

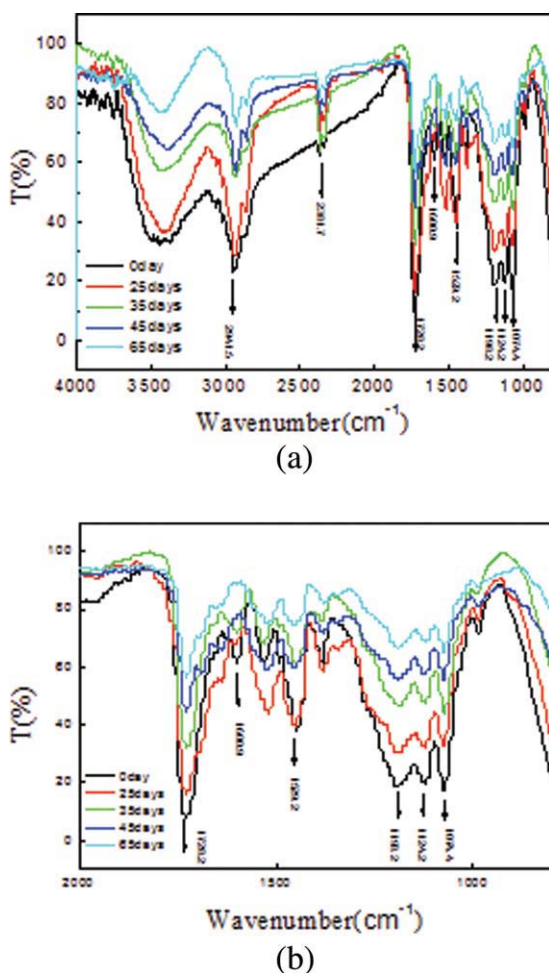


**Figure 5** Resistance of composite coating changes with time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the molecular structure changes within the coatings by ultraviolet irradiation. To confirm the effect of UV irradiation on coating failure process, FTIR analysis was carried out for the polyurethane topcoat after the samples were exposed in 3.5% NaCl solution + UV environment for different times. The results are shown in Figure 6. Figure 6(a) is the full spectra and Figure 6(b) shows some enlarged parts.

In Figure 6, the absorption peak at  $1728.2 \text{ cm}^{-1}$  is formed by the overlapping C=O peaks in ester and carbamate, the peak at  $1600.9 \text{ cm}^{-1}$  is due to the stretching vibrations of  $-\text{NH}-\text{COO}-$ , the peak at  $1529.3 \text{ cm}^{-1}$  is due to the deformation vibration of the characteristic  $-\text{NH}$  band in *sec*-amide, the peaks at  $2941.5 \text{ cm}^{-1}$  and  $1453.7 \text{ cm}^{-1}$  are due to the stretching vibration and bending vibration of  $-\text{CH}_3$ , the peak at  $1198.2 \text{ cm}^{-1}$  is the C–N stretching vibration absorption peak, and peaks at  $1124.0 \text{ cm}^{-1}$  and  $1074.4 \text{ cm}^{-1}$  are the C–O stretching vibration absorption peaks.<sup>18–20</sup>

The chemical structure of polyurethane is  $-\text{R}'\text{OOC}-\text{NH}-\text{R}-\text{NH}-\text{COO}-$ .<sup>19</sup> From Figure 6 it is seen that under the action of UV irradiation, in aliphatic polyurethane the absorption peaks of  $-\text{NH}-\text{COO}-$ , C=O, C–N, and C–O gradually decreased, which means that C–N and C–O bonds in the coating fractured under UV irradiation. The studies on mechanism of polyurethane degradation by UV showed that,<sup>7,9</sup> the dissociation energies for C–O and C–N bonds are respectively, 120–300 KJ/mol and 314–335 KJ/mol. The energy of UV light used in this experiment was 382 KJ/mol, which is sufficient to lead to fracture of C–O and C–N bonds in aliphatic polyurethane. It may be seen that after 25 days of exposure in 3.5% NaCl solution with UV, the absorption peaks of C=O, C–N, and C–O all attenuated to some extent. However, more obvious decreases for strength of the absorption peaks occurred from 25th day to 35th day. This is consistent to the change of coating resistance shown



**Figure 6** IR spectra of the aliphatic polyurethane topcoat in the composite coating before and after failure, (a) the whole spectra, (b) the enlarged parts. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

in Figure 4, indicating that in the later period of testing the degradation of polymer molecules resulted in quick decrease of the coating resistance. The breaking of polymer bonds increased the porosity and caused more channels in the coatings, which accelerated permeation of electrolyte in coating and corrosion of the substrate under coating.

In the later testing time, the  $\text{—NH—COO—}$  absorption peak gradually decreased until disappeared, while  $\text{C=O}$ ,  $\text{C—N}$ , and  $\text{C—O}$  absorption peaks continued to decay to very weak. The fracture of  $\text{C—N}$  bond may generate amino and alkyl free radicals, releasing  $\text{CO}_2$ . The fracture of  $\text{C—O}$  bond generates carbamoyl and alkyl free radicals, while the carbamoyl radicals break down into amino free radicals and  $\text{CO}_2$ .<sup>21</sup> Therefore, during the later stage of the testing the polyurethane coating seriously degraded and even pulverized.

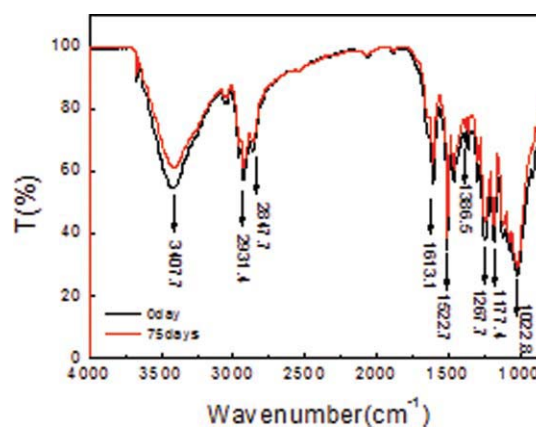
FTIR analysis was further carried out for the micaeous iron oxide epoxy intermediate coat before

immersion and after the immersion in 3.5% NaCl solution under UV for 75 days. The results are shown in Figure 7.

In Figure 7, the broad and strong absorption peak at  $3407.7\text{ cm}^{-1}$  is formed by the  $\text{—OH}$  stretching vibration of hydroxyl, the peak at  $2847.7\text{ cm}^{-1}$  and  $2931.4\text{ cm}^{-1}$  are due to the stretching vibrations of methylene and methyl, the four absorption peak between  $1386.5\text{ cm}^{-1}$  and  $1613.1\text{ cm}^{-1}$  are due to the stretching vibration of benzene ring skeleton  $\text{C=C}$ , the peaks at  $1267.1\text{ cm}^{-1}$  is the bending vibration of  $\text{O—H}$  in phenol, the peak at  $1177.4\text{ cm}^{-1}$  is the vibration angle of  $(\text{CH}_3\text{—C—CH}_3)$  structure in double A and isopropyl, and peaks at  $1022.8\text{ cm}^{-1}$  are due to the  $\text{C—N}$  stretching vibrations.<sup>22</sup>

It is seen from Figure 7 that, because of the barrier effect of the topcoat, the middle coat was not influenced significantly by UV radiation. Each absorption peak in the infrared spectrum did not attenuate obviously after immersion for 75 days.

From above results, the effect of ultraviolet irradiation on failure process of aliphatic polyurethane composite coatings may be divided into two stages. In the early stage, the decrease of coating performance is mainly due to the rapid permeation of electrolyte solution and the increased coating porosity by the evaporation of residual solvents at increased temperature. In this stage the coating still behaves as a good protection layer. With the testing time extended, the effect of UV irradiation plays a dominant role in degradation of the coating. In the later stage, more  $\text{C—N}$  and  $\text{C—O}$  bonds rupture under UV action, leading to quick increase of coating porosity and decrease of coating resistance. As the result, the composite coatings were quickly permeated through and metal corrosion under the coating begins. In the last time of testing, also the pores in coatings may be partly blocked by corrosion



**Figure 7** IR spectra of the micaeous iron oxide epoxy intermediate coat in the composite coating before and after failure. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

products and the decreasing rate of coating resistance reduces, the low coating resistance, corrosion of the substrate and pulverization from the surface cause failure of the composite coatings.<sup>23</sup>

### CONCLUSIONS

UV irradiation significantly accelerated the failure process of inorganic zinc-rich/micaceous iron oxide epoxy/aliphatic polyurethane composite coating in 3.5% NaCl solution. The failure process of the coating system in 3.5% NaCl solution + UV may be divided into two stages: In the early stage, the thermal effect generated by the ultraviolet irradiation is the main reason leading to the increase in coating porosity, but this effect is not serious and the coating remains high impedance and good protection ability. In the latter stage, the fracture of polymer chains in the top coating by UV irradiation is the main factor resulting in quick decrease of coating performance. C—N and C—O bonds in polyurethane coating are broken by UV irradiation, leading to quick increase of coating porosity and quick decrease of coating resistance.

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