

Effect of ZnO nanoparticles on anti-aging properties of polyurethane coating

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Polyurethane nano-coatings were prepared by adding nano-concentrates with nanometer zinc oxide (nano-ZnO) to polyurethane coating. The dispersion state of nanoparticles was observed by TEM images. SEM observation and FT-IR analysis indicate that the nano-coating with 1% ZnO nanoparticles can retain better morphological structure than the nano-coating with 5% ZnO nanoparticles after 500 h accelerated aging. It is known from XPS analysis that the anti-oxidation properties of polyurethane coating are enhanced by 1% ZnO nanoparticles through the nano-network and destroyed by 5% ZnO nanoparticles due to the strong light catalysis. A small change in capacitances of nano-coatings with 1% ZnO nanoparticles before and after accelerated aging indicates that 1% ZnO nanoparticles improve the corrosion resistance of coating, while a large increase in capacitances of nano-coating with 5% ZnO nanoparticles before and after accelerated aging demonstrates that 5% ZnO nanoparticles damage the corrosion resistance of coating.

ZnO nanoparticles, nano-concentrates, polyurethane nano-coating, accelerated aging, resistance to weathering

The aircraft coatings should provide an efficient protection for aircraft during the whole service life. The long-term weathering durability and corrosion resistance are required for the aircraft coatings. When the aircraft coatings are destroyed and cannot meet the anti-aging and anti-corrosion requirements, the aircraft coatings need to be completely reapplied. The relative cost for the treatment is very huge. In recent decades, the accidents caused by aircraft corrosion have reminded researchers of importance of the study. The epoxy and polyurethane coatings are usually used as the protective primer and topcoat of aircraft. However, the resistance of these traditional coatings to weathering and corrosion is not very satisfactory after long-time outdoor corrosion exposure^[1–3].

The objective of this study is to develop a highly protective aircraft nano-coating. Firstly, we select aliphatic polyurethane system that has better resistance to UV radiation than aromatic polyurethane system. Although aliphatic polyurethane coating has good resistance to

UV radiation, its resistance to humidity and corrosive mediums needs to be enhanced. Development of nano-science and nano-technology provides a modification way for the specific requirement of the coatings^[4–6].

Nano-coating has attracted a lot of attention as a simple and cost-effective method of enhancing coating properties by the addition of a small amount of properly designed and dispersed nanometer fillers. Zhou et al.^[7] investigated the change of the properties of acrylic-based polyurethane via the addition of nano-silica. Yang et al.^[8] studied the effects of P/B on the properties of anticorrosive coatings with different particle sizes. Jalili et al.^[9] investigated the variations in properties of 2-pack polyurethane clear coat through separate incorporation of hydrophilic and hydrophobic nano-silica. In this work, nano-concentrates containing ZnO nanoparticles were

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developed and applied to polyurethane coatings for improving the corrosion-resistant and anti-aging properties of aircraft coating.

The goal of weathering test is to predict whether or not a coating is durable enough to satisfy the service life demand. A disadvantage of natural outdoor exposure is that it will take years to obtain meaningful results. A variety of acceleration weathering techniques are developed and utilized to investigate the weathering and degradation of coatings. These accelerated test methods attempt to accelerate the natural environments with high UV radiation, humidity, elevated temperature and gaseous pollutants. Thus, the coating performance can be estimated in a short test period.

Traditional methods such as measurement of weight loss and gloss loss are used to examine the weathering of coatings during the past decades. However, these traditional methods are not adequate to understand the coating degradation. The coating degradation is a combination of both chemical and physical processes. Several fine techniques such as XPS, FTIR, SEM and EIS are used to investigate the chemical degradation of the polymer coatings^[10,11]. Based on the observation and analysis, we discuss the degradation of polyurethane coatings, and study the effect of different content of ZnO nanoparticles on anti-aging and corrosion-resistant properties of the coatings.

1 Experimental

1.1 Material

The samples were two-component, solvent-based polyurethane coatings prepared from a-365 acrylic resin with 2.9 wt% OH groups from Bayer Co. and N-75 HDI based aliphatic polyisocyanate with 16.5 wt% NCO groups from Bayer Co. HDI based aliphatic polyisocyanate was used as a hardener of acrylic resin, and the ratio of NCO/OH is 1.2. Zinc oxide nanoparticles with primary particle size of (20±5) nm (MR, from Zhoushan Nanomaterial Co.) were used as the nanometer modification filler of coatings. The block copolymer dispersing agent (HX-4800, from Huaxia Additives Chemicals Co.) as the surface stabilizer of nanoparticles was received.

1.2 Sample preparation

Firstly, 0.05–0.1 g copolymer dispersing agents were added to 30 g toluene, and then 6 g ZnO nanoparticles were added to the solution and dispersed at 25°C for 60

min by ultrasonic wave to obtain nano-solution. Finally, the nano-solution was centrifuged at 2×10^4 r/min for three times until the non-precipitation materials were found in the solvent. The final product is nano-concentrate. Weight percent of ZnO nanoparticles in the nano-concentrate is 50 wt%. The acrylic resins were cured with HDI based aliphatic polyisocyanate to obtain No1 coating without nanoparticles. Nano-concentrates were added to acrylic resin, and then the mixed materials were cured with hardener to obtain No2 nano-coating with 1 wt% ZnO nanoparticles and No3 nano-coating with 5 wt% ZnO nanoparticles, respectively.

The primer and topcoat used in this study were epoxy-polyamide coating and polyurethane coating, respectively. The coatings were applied by spreading aluminum alloy plates, and the thickness of the primer and topcoat was 20 μm and 30 μm, respectively.

1.3 Accelerated aging test

The accelerated aging test provides a solid reference for practical weathering of coatings in natural environment. The SH60CA weatherometer was used for laboratory simulation of the damaging effects of natural weathering. The accelerated aging test was conducted in the chamber by ASTM D529 Standard. The test was based on cycles of water spray and drying (spraying water 18 min per 2 h) at $(50 \pm 5)^\circ\text{C}$ with exposure to UV-radiation. The coated plates were exposed with a slope of 18° to horizontal plane. The accelerated aging test of coatings was performed for 500 h, and the chemical changes of coatings before and after accelerated aging were analyzed.

1.4 Characterization techniques

The distribution of nanoparticles was examined with a JEM-2000EX TEM (transmission electron microscopy) running at an acceleration voltage of 200 kV. TEM samples were prepared by spreading a small amount of nano-concentrates on a TEM grid. The SEM (scanning electron microscopy) micrographs of samples were analyzed with an XL30 ESEM instrument, and the imaging analysis was operated at 20 kV. A gold film was sprayed atop the surface of specimen to make it electrically conductive. The FT-IR (Fourier transform infrared spectroscopy) spectra were collected by means of a Perkin-Elmer 2000FT-IR spectrometer from 4000 to 500 cm^{-1} . XPS (X-ray photoelectron spectroscopy) analysis was performed with a Thermo VG ESCALAB250 spectrometer to study the element composition of the sample

surface, using AlK_{α} excitation radiation ($h\nu=1486.6$ eV). EIS test was performed using a Princeton Applied Research EG&G 273 potentiostat/galvanostat and an EG&G 5210 lock-in amplifier integrated with a M352 corrosion software. The test was used to analyze the corrosion resistance of coatings during immersion in 3.5% NaCl solution. Impedance spectra of the samples in different immersion times were recorded in the 10^{-2} – 10^5 Hz frequency range, with sinusoidal alternating potential signal of 10 mV. The measurements were conducted using three electrodes system with a coated substrate as working electrode, a platinum plate as auxiliary electrode and a saturated calomel electrode as reference electrode. The test was performed for 450 h.

2 Results and discussion

2.1 Dispersion mechanism of nanoparticles

A great many of millimeter fillers are added to binders to improve the general properties of polyurethane coatings. These millimeter fillers and binders cannot form a whole network system, whereas nanometer fillers can form an interpenetrating network structure that enhances corrosion resistance. Therefore this work mainly investigates the effect of nanometer fillers on the coating properties.

The TEM image in Figure 1 shows a high dispersion extent of ZnO nanoparticles with a dimension of 20–50 nm. The enclosing materials on the surface of nanoparticles indicate a good chemical absorption between copolymer dispersing agents and nanoparticles.

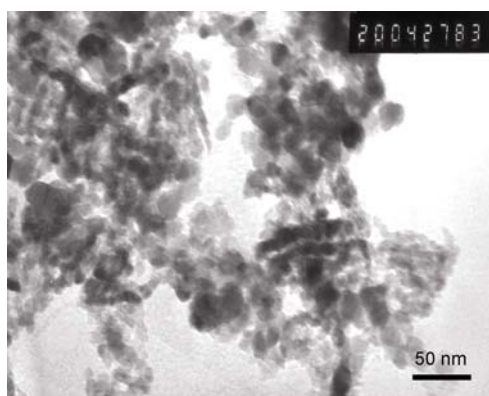


Figure 1 TEM image of ZnO nanoparticles modified by copolymer dispersing agents.

Surfaces of the nanoparticles usually contain a high concentration of unsaturable bonds and hydroxyl groups. The hydrogen bonds that are easily formed from these

hydroxyl groups by Van der Waals force lead to aggregation of nanoparticles. Consequently, the excellent properties of nanoparticles are difficult to play. When the nanoparticles are added to polymer or coating, they increase the total energy of the system. Because the process is not spontaneous and the system is very unstable, some dispersing agents must be added to the system to decrease the interface force and total energy. The copolymeric dispersing agents have two key parts to their structure, an anchoring group that absorbs onto the surface of nanoparticles and a polymeric chain that keeps the nanoparticles apart. Different anchor groups of copolymer dispersing agent can absorb on the surfaces of different nanoparticles by only tail absorption. Thus, the copolymer dispersants can greatly improve the dispersion effect of nanoparticles^[12,13].

2.2 SEM morphologies

The effect of nanoparticles on the morphologies of three coatings before accelerated aging is very small, and hence the SEM analysis mainly studies the morphology variation of three coatings after accelerated aging. SEM morphologies of coatings after accelerated aging are shown in Figure 2. The several deep cracks are presented in No1 coating in Figure 2(a), while only some small craters are randomly distributed on the surface of No2 coating in Figure 2(b). Those deep cracks severely destroy the anti-corrosion performance of No1 coating. The depth of small craters on the surface of No2 coating is in the range of 20–80 nm, which is only about 1/1000 of the coating thickness. The existence of these small craters does not obviously affect the performance of No2 coating. In Figure 2(c), a great number of deep cracks and craters are distributed in No3 coating, resulting in the severe damage of the coating performance. These micro-cracks may be attributed to the shrinkage and breakage of No1 coating and No3 coating under UV radiation and the external stress is generated by temperature/humidity cycling. When the polyurethane polymer is exposed to high UV environment, UV radiation provides energy to initiate the degradation of the polymer. In the presence of oxygen, moisture and pollutants, the polyurethane polymer is easily oxidized. The degradation and oxidation of polymer produce some defects on the surface of the coating^[14–16]. The soluble degradation products can penetrate into these defects of the coating along with water, and then it is difficult for them to escape from the polymer network. Thus, the

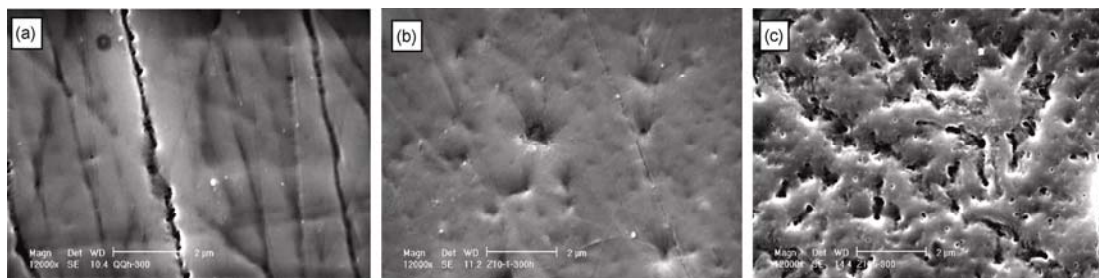


Figure 2 SEM morphologies of No1 coating (a), No2 coating (b) and No3 coating (c) after 500 h accelerated aging.

accumulation of degradation products in the weathering cycling causes an osmotic pressure effect in the coating structure, resulting in cracking of coating.

The film of No2 coating is continuous, whereas the film of No3 coating is separate and has some visible big voids on the surface. Apparently, the film of No2 coating with 1% ZnO nanoparticles has a better barrier effect than that of No3 coating with 5% ZnO nanoparticles. The high content of ZnO nanoparticles easily initiate the light catalysis for polyurethane polymer, and the light catalysis leads to scission of carbon chain and breakage of ether bond of polyurethane polymer. Therefore, the anti-corrosion properties of No3 coating are damaged by 5% ZnO nanoparticles.

2.3 FT-IR analysis

The functional groups of polymers can be evaluated

from infrared spectroscopy. The variation with the functional groups of polyurethane polymers before and after accelerated aging is shown in Figures 3 and 4. The absorption peak at 2260 cm^{-1} is assigned to the residual isocyanate groups (NCO). In Figure 4, the high peak intensity of isocyanate groups of No3 coating before aging at 2260 cm^{-1} indicates that the isocyanate groups and hydroxyl groups are not fully cured. This is because 5% ZnO nanoparticles damage the curing reaction of isocyanate groups and hydroxyl groups. A drastic reduction in the peak intensity of isocyanate groups of No3 coating after accelerated aging is attributed to the reaction of isocyanate groups and residual hydroxyl groups on the surface of ZnO nanoparticles during accelerated aging. In Figure 3, the peak intensity of isocyanate groups of No2 coating after aging is similar to that of No2 coating before aging. This demonstrates that 1%

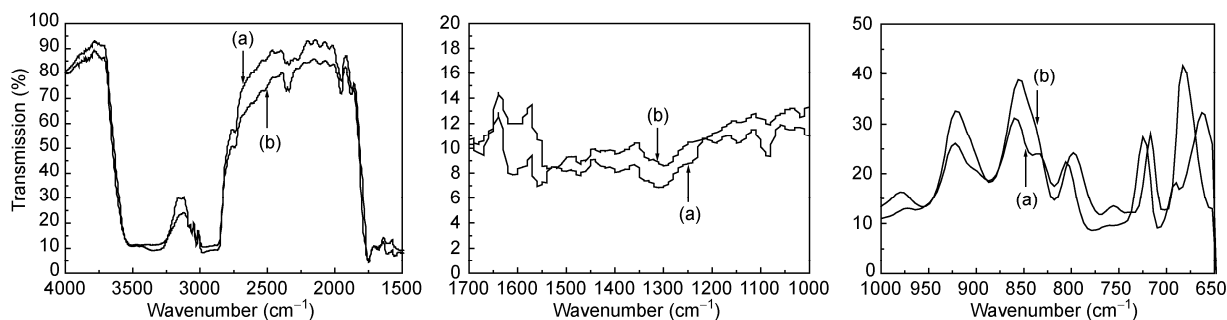


Figure 3 FT-IR spectra of No2 coating before (a) and after (b) 500 h accelerated aging.

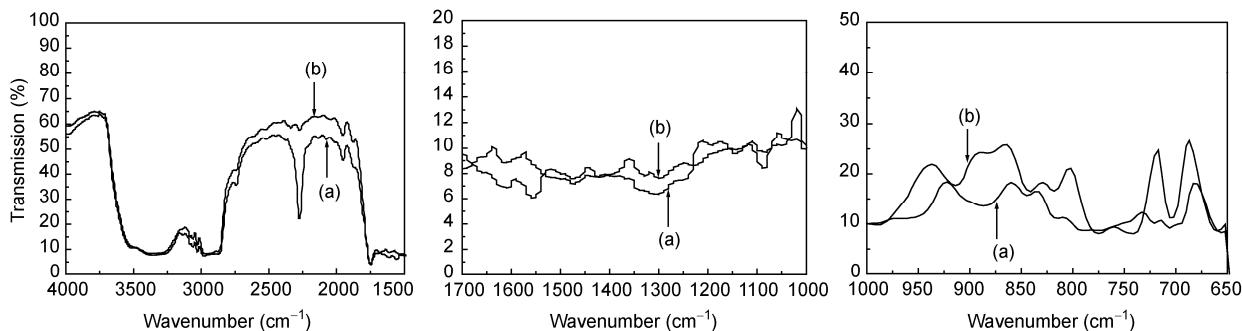


Figure 4 FT-IR spectra of No3 coating before (a) and after (b) 500 h accelerated aging.

ZnO nanoparticles do not negatively affect curing reaction of polyurethane polymer.

The absorption peak at 1550 cm^{-1} indicates the presence of NHCO groups that is obtained from reaction of OH groups and NCO groups. The peak intensity of NHCO groups of No2 coating does not change obviously before and after accelerated aging, whereas that of No3 coating weakens drastically after 500 h accelerated aging. A decline in the peak intensity of NHCO groups is attributed to the damage of polyurethane structure, which destroys the weathering resistance of No3 coating. It is concluded that 1% ZnO nanoparticles improve the resistance of NHCO groups to weathering, whereas 5% ZnO nanoparticles initiate the scission of NHCO groups during weathering.

The degradation of polyurethane polymer by UV light is a multi-stage process involving initiation, propagation and termination phases. When some groups of the polymer absorb UV light, the electronic energy of molecules increases, and the excited molecules initiate the bond cleavage with the production of free radicals. These highly reactive species can react with oxygen to form the peroxy-free radicals. When these radicals attack the polymer, they abstract hydrogen atoms from the polymer, and form a hydroperoxide and a new carbon

centered radical. The degradation proceeds until two kind of free radicals recombine in the termination step^[17,18]. It is seen from FT-IR analysis that the nano-network formed from 1% ZnO nanoparticles weakens the trend of bond cleavage and relative degradation of coatings. Therefore, the effective nano-network improves the anti-aging properties of No2 coating.

2.4 XPS analysis

In order to better understand the chemical reaction occurring on the coating surfaces during weathering, XPS technique is employed for surface analysis of polyurethane coatings. The C1s, O1s, N1s and Zn2p spectra of No1 coating before and after accelerated aging are shown in Figures 5 and 6. Tables 1–6 list the relative XPS results obtained from coatings. The C1s, N1s and O1s XPS peak of No1 coating before accelerated aging is at about 288, 403 and 535 eV in Figure 6, respectively. C, N and O element content of No1 coating before accelerated aging is 78.33%, 2.23% and 19.44% in Table 1, respectively, while that of No1 coating after 500 h accelerated aging is 67.9%, 3.26% and 28.85% in Table 2, respectively. UV radiation can initiate the scission of molecular chain and degradation of polymer. The loss of carbon of coatings may be caused by the migration and

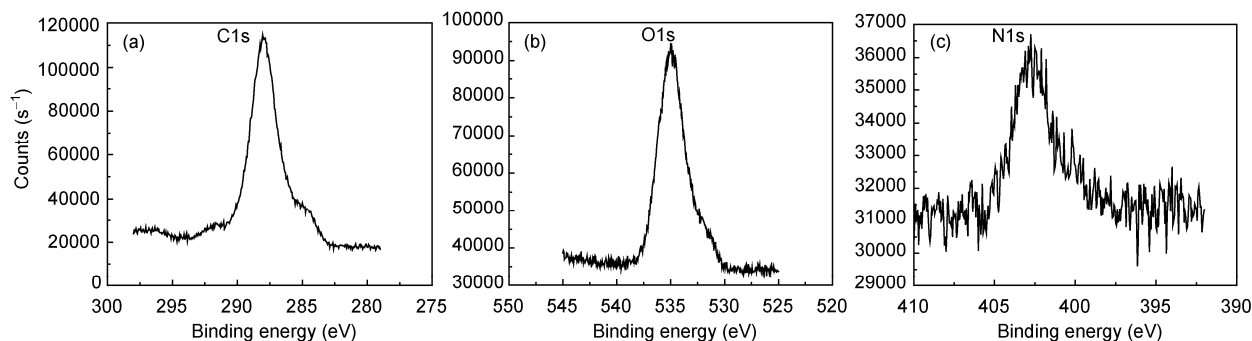


Figure 5 XPS spectra of No1 coating before accelerated aging. (a) C1s; (b) O1s; (c) N1s.

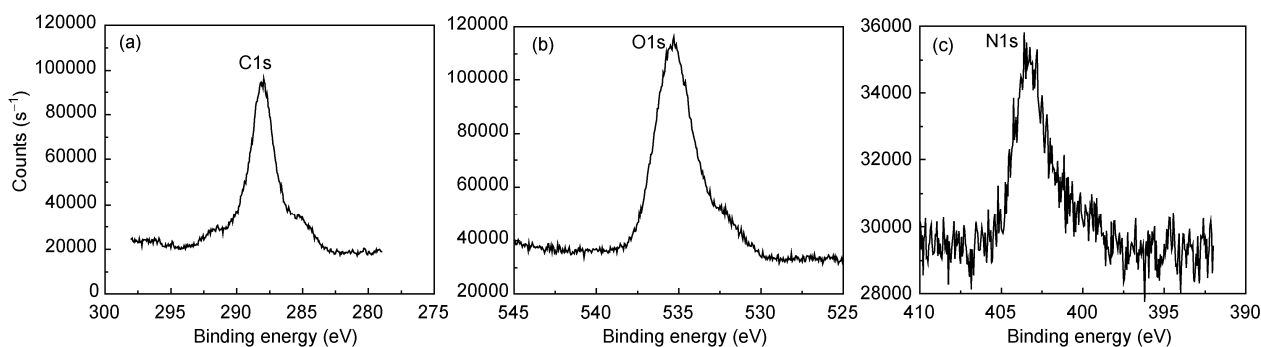


Figure 6 XPS spectra of No1 coating after 500 h accelerated aging. (a) C1s; (b) O1s; (c) N1s.

Table 1 Element composition of No1 coating before accelerated aging

Element	Start BE	Peak BE	End BE	Height counts	Area (N)	At. (%)
C1s	293.45	287.96	282.35	92890.38	1.79	78.33
N1s	406.10	402.81	396.50	4905.11	0.05	2.23
O1s	539.15	535.01	529.25	58451.63	0.44	19.44

Table 2 Element composition of No1 coating after 500 h accelerated aging

Element	Start BE	Peak BE	End BE	Height counts	Area (N)	At. (%)
C1s	293.10	287.97	283.10	73472.63	1.34	67.90
N1s	406.70	403.46	397.05	5788.22	0.06	3.26
O1s	538.45	535.28	529.50	78269.36	0.57	28.85

Table 3 Element composition of No2 coating before accelerated aging

Element	Start BE	Peak BE	End BE	Height counts	Area (N)	At. (%)
C1s	294.80	288.99	282.75	87171.04	1.84	77.51
N1s	406.85	403.60	398.55	8888.33	0.09	3.72
O1s	539.15	535.29	529.75	55968.04	0.44	18.53
Zn2p	1032.20	1025.10	1016.20	2887.65	0.01	0.25

Table 4 Element composition of No2 coating after 500 h accelerated aging

Element	Start BE	Peak BE	End BE	Height counts	Area (N)	At. (%)
C1s	293.45	287.20	282.05	124487.30	2.33	75.43
N1s	405.50	402.18	396.80	15300.13	0.14	4.49
O1s	538.75	534.22	529.30	88940.94	0.62	20.07
Zn2p	1030.45	1023.73	1018.30	3459.77	0	0.01

Table 5 Element composition of No3 coating before accelerated aging

Element	Start BE	Peak BE	End BE	Height counts	Area (N)	At. (%)
C1s	294.30	287.89	282.75	180060.80	2.89	83.56
N1s	406.85	402.71	398.50	4971.42	0.04	1.14
O1s	540.00	534.65	529.60	80491.38	0.51	14.89
Zn2p	1030.46	1023.41	1018.47	12710.36	0.01	0.42

Table 6 Element composition of No3 coating after 500 h accelerated aging

Element	Start BE	Peak BE	End BE	Height counts	Area (N)	At. (%)
C1s	293.70	288.24	282.75	112544.70	2.20	71.32
N1s	406.65	402.91	397.55	9782.31	0.09	3.25
O1s	538.90	534.79	529.50	83071.54	0.58	25.06
Zn2p	1029.59	1024.04	1016.91	8369.62	0.01	0.37

volatility of oxidation products obtained from the degradation of carbonaceous compounds. The XPS peaks at 287.96 eV in Figure 5(a) is assigned to either carboxyl groups (COO) produced during the coating oxidation or $\text{HN}-\text{C}=\text{O}$ groups obtained from urethane or urea. It is found that the C1s peak intensity of No1 coating in Figure 6(a) decreases after 500 h accelerated test. Since COO groups are not stable, the reduction of C1s peak intensity is caused by the formation and loss of oxidation products on the coating surface^[19-21]. The nitrogen-to-carbon (N/C) and oxygen-to-carbon (O/C) ratio

of No1 coating before accelerated aging is 1/35.13 and 1/4.03, respectively, whereas that of No1 coating after accelerated aging is 1/20.83 and 1/2.35, respectively. The increase of N/C and O/C ratio indicates that No1 coating degrades during weathering, and the degradation causes the inefficiency of coating.

In Tables 3 and 4, C and O element content of No2 coating before accelerated aging is 77.51% and 18.53%, respectively, and C and O element content of No2 coating after 500 h accelerated aging is 75.43% and 20.07%, respectively. The carbon-to-oxygen (C/O) ratio of No1

coating after aging decreases from 4.03 of No1 coating before aging to 2.35, whereas the C/O ratio of No2 coating after aging only decreases from 4.18 of No2 coating before aging to 3.76. The high C/O ratio of polymers or coatings is directly connected with the good anti-oxidation and resistance to weathering. The high C/O ratio of No2 coating after aging demonstrates that 1% ZnO nanoparticles effectively resist the weathering damage to the molecular chain of polyurethane coating.

In Tables 5 and 6, XPS spectra and element content of No3 coating before and after accelerated aging are illustrated, respectively. The C/O and C/N ratio of No3 coating before aging is 5.61 and 73.30, respectively, and the C/O and C/N ratio of No3 coating after accelerated aging is 2.85 and 21.94, respectively. The C/O reduction percentage of No1 coating, No2 coating and No3 coating after 500 h accelerated aging is 41.69%, 10.05% and 49.20%, respectively. Therefore, the anti-aging properties of No2 coating are the best among three coatings, and anti-aging properties of No3 coating are the worst among three coatings. Zn content of No2 coating after aging drastically decreases from 0.25% of No2 coating before aging to 0.01%, whereas Zn content of No3 coating after aging only decreases from 0.42% of No3 coating before aging to 0.37%. The strong photo-catalytic effects of 5% ZnO nanoparticles on the surface of No3 coating cause the degradation and damage of network structure of polymer surface, which leads to a declination in C content and an increase in O content and Zn content on the coating surface. 1% ZnO nanoparticles cannot effectively produce the negative photo-catalytic effects on the surface structure of No2 coating.

2.5 EIS analysis

Two equivalent circuits are shown in Figure 7, where R_s denotes the solution resistance, C_c and R_c the electric capacitance and resistance of the coating, respectively; C_{dl} and R_{ct} represent the double-layer capacitance and the charge transfer resistance at the interface of coating and substrate. Figure 7(b) is used as the equivalent circuit of the coating systems in this study. The variation of capacitances for coatings before and after accelerated aging is shown in Figures 8–10. The capacitances of coatings can be used for the prediction of long-term anti-corrosion performance. Water diffusion in an organic coating is connected with the time dependence of coating capacitance. The capacitance variation can reflect the decay of coating performance with exposure

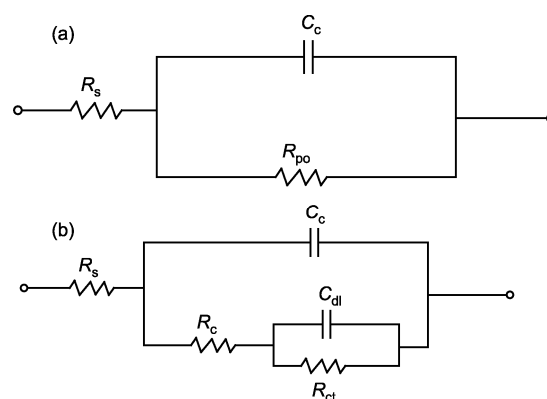


Figure 7 Equivalent electrical circuits.

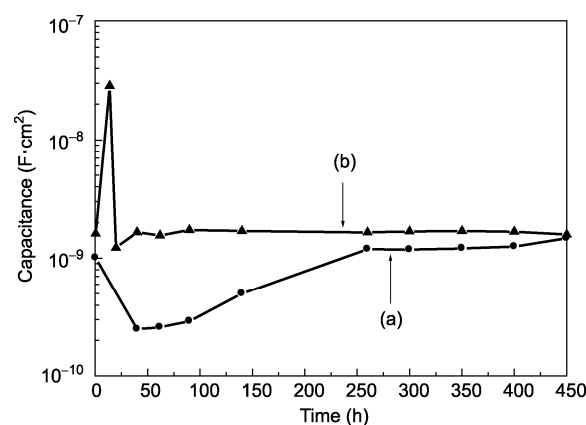


Figure 8 Variation of capacitances for No1 coating before (a) and after (b) 500 h accelerated aging.

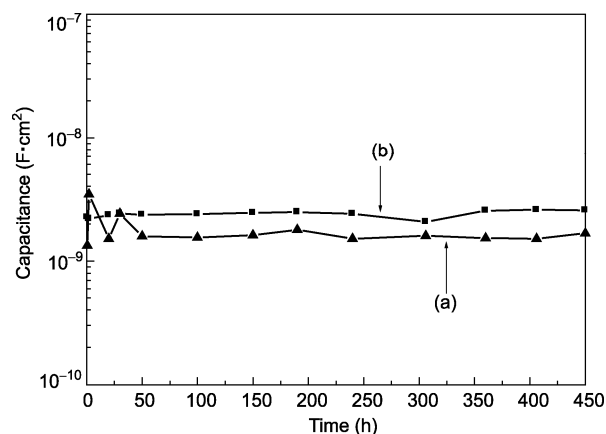


Figure 9 Variation of capacitances for No2 coating before (a) and after (b) 500 h accelerated aging.

time^[22–25].

The capacitances of three coatings all show the increasing trend after accelerated aging. At first 250 h of the test, the difference between capacitances of No1 coating before and after accelerated aging is very big (approximately $1.408 \times 10^{-9} \text{ F} \cdot \text{cm}^2$). At 250–450 h of the test, their difference decreases and trends to be a

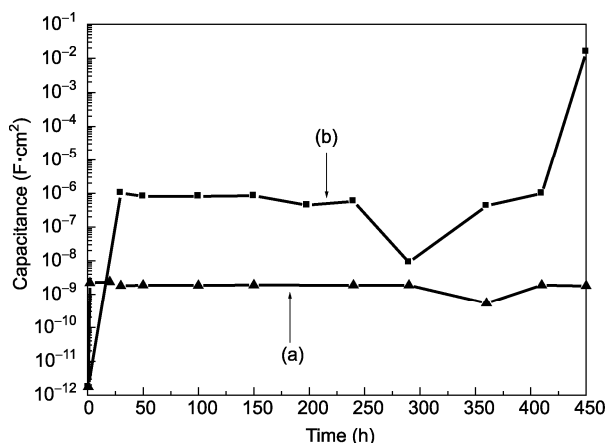


Figure 10 Variation of capacitances for No3 coating before (a) and after (b) 500 h accelerated aging.

specific value ($5 \times 10^{-10} \text{ F} \cdot \text{cm}^2$). These changes are presented in Figure 8. In Figure 9, the smooth line of No2 coating indicates that water diffuses in a homogeneous way. The difference in capacitances of No2 coating before and after accelerated aging is relatively fixed and small (about $7 \times 10^{-10} \text{ F} \cdot \text{cm}^2$), which demonstrates that 1% ZnO nanoparticles enhances the corrosion resistance of polyurethane coating. This is because 1% well-distributed ZnO nanoparticles can form an interpenetrating nano-network that exerts “labyrinth” effect on the coating. The interpenetrating nano-network can shield the penetration of corrosive mediums through the “labyrinth” effect. It is found that the capacitances of No3 coating before accelerated aging change with two distinguishing stages in Figure 10. The rapid increasing capacitance of No3 coating in the initial period of immersion suggests that water can easily permeate into the coating structure through the micro-pores. After 24 h of immersion, the permeation process in No3 coating before accelerated aging reaches a relatively stable state. However, the capacitances of No3 coating before and after accelerated aging show a very dramatic difference (about $8 \times 10^{-7} \text{ F} \cdot \text{cm}^2$), which is attributed to the sharp declined anti-corrosion performance of No3 coating during accelerated aging. The difference in capacitances of No3 coating before and after aging is higher than that of No1 coating and No2 coating before and after aging. The big difference in capacitances of No3 coating before

and after accelerated aging indicates that 5% ZnO nanoparticles damage the corrosion resistance of No3 coating due to the photo-catalytic effect and aggregation effect of nanoparticles.

3 Conclusions

The anchor groups and long carbon chains of copolymer dispersing agent prevent the aggregation of nanoparticles by spatial steric effect, so the nanoparticles can be well distributed in the coating. The micro-cracks generated by UV radiation and the external stress during weathering cause the morphological damage of polyurethane coating. During the accelerated aging, polyurethane coating with 1% ZnO nanoparticles demonstrates better morphological structure than polyurethane coatings without ZnO nanoparticles and with 5% ZnO nanoparticles. The FT-IR peak intensity of NHCO groups at 1550 cm^{-1} of polyurethane coating with 5% ZnO nanoparticles drastically weakens after aging, while that of polyurethane coating with 1% ZnO nanoparticles has a very small change before and after aging. A reduction in FT-IR peak intensity of NHCO groups is due to the degradation of polyurethane coating. The coating oxidation and degradation during accelerated aging causes the reduction of the C/O ratio and C1s XPS peak intensity. The high C/O ratio of polyurethane coating with 1% ZnO nanoparticles is connected with the good resistance to weathering, and the low C/O ratio of polyurethane coating with 5% ZnO nanoparticles is attributed to the poor anti-aging performance. EIS analysis shows that the difference between capacitances of polyurethane coatings with 5% ZnO nanoparticles before and after aging is the biggest, and the difference between capacitances of polyurethane coatings with 1% ZnO nanoparticles before and after aging is the smallest among three coatings. This demonstrates that 1% ZnO nanoparticles enhance the resistance of coating to permeation of corrosive mediums. It is concluded from the analysis that nano-size network formed by 1% ZnO nanoparticles improves the resistance of coating to weathering and corrosion, and 5% ZnO nanoparticles have a negative effect on the coating performance due to light catalysis and aggregation of nanoparticles.

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