

Short Communication

Corrosion Behavior of Carbon Nanotubes/Polyurea Composite Coatings in Alkaline Environment

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The carbon nanotubes (CNTs) were doped into polyurea for the test of Shore hardness and the adhesion on the aluminum alloy substrate. The corrosion resistance of carbon nanotube/polyurea composite coatings was investigated by electrochemical impedance spectroscopy (EIS) in 0.1 mol/L NaOH solution for 21 days. The results showed that the surface hardness of polyurea was significantly improved after doping with CNTs while the adhesion to aluminum alloy substrate was slightly improved. The coating equivalent capacitance (R_c) and charge transfer resistance (R_{ct}) of the polyurea coating added with CNTs were larger than the pure polyurea coating during immersion, indicating that adding CNTs can provide better protection to the aluminum alloy substrate. The relationship between the doping amount of carbon nanotubes and corrosion resistance is $1.0 \text{ wt.}\% > 0.5 \text{ wt.}\% > 0 \text{ wt.}\%$.

Keywords: polyurea, carbon nanotubes, adhesion, EIS, corrosion resistance

1. INTRODUCTION

Polyurea elastomer coatings are environmentally friendly materials with many desirable properties such as rapid cure, high adhesion, wide temperature tolerance, and excellent corrosion resistance [1]. Consequently, polyurea coatings have been widely used in the construction, chemical and transport industries, e.g. for the protection of concrete, metal and other substrates. Nanomaterials possess unique physical and chemical properties due to their size, shape and structure which have enabled advances in the performance of materials for catalysis, electronics and energy-based research [2]. Consequently, the doping of nanomaterials to the organic coating will improve the mechanical properties [3], anti-corrosion performance [4], thermal stability [5] and wear resistance [6].

When nano-SiO₂ is doped into the polyurea coating, its hardness, UV aging resistance and corrosion resistance are significantly enhanced [7]. Adding nanomaterials to the polyurea coating gives a network of flocculent fillers that could enhance the strength and toughness of the material [8].

However, the poor dispersibility and interfacial bonding of CNTs limits its reinforcing effect on the polymer [9]. The nitric acid oxidation of CNTs results in the formation of carboxyl groups on the surface of the CNTs, which under air oxidation form hydroxyl groups [10]. The hydroxy CNTs can be combined with the isocyanate in the polyurea to form a urethane bond, which enhances the material properties. The use of epoxidized multi-walled carbon nanotubes (MWCNTs) as reinforcing agents can improve the mechanical properties of polyurea nanocomposites [11].

When the polyurea coating is soaked in sodium hydroxide solution, its tensile strength is reduced by 25% and the elongation at break is increased by 9.6%. Compared with salt spray aging and seawater immersion, the corrosion resistance of the coating in strong alkali solution will decrease [12]. When an electrochemical reaction occurs at the coating/metal interface, the bond between the coating and the substrate is weakened, causing the coating to bubble or peel off. [13]. When the base metal undergoes an electrochemical reaction, the pH of the cathode region is increased to 13-14, and the pH of the stripping zone is higher than 14 [14]. Therefore, it is important to study the corrosion resistance of the coating in alkali environment. In addition, the study of the system in an alkaline environment will have some reference value for its application in concrete.

In this study, hydroxyl CNTs were doped into the polyurea coating. The Shore hardness of the different coatings and the adhesion to the aluminum substrate were tested. The EIS of the composite coating/aluminum alloy system in 0.1 mol/L NaOH solution was tested. The corrosion resistance of the coating in alkali environment was evaluated according to the characteristics of the EIS and the impedance modulus at low frequencies.

2. EXPERIMENTAL

2.1. Coating preparation

The substrate is made of 7050 aluminum alloy sheet and the size is 100*100*3 mm. The substrate was degreased by acetone, ultrasonically cleaned and grounded with 800 # sandpaper. The specific preparation steps are as follows: heating polyurea component A (isocyanate) to 80 °C; adding a certain proportion of aminated carbon nanotubes; ultrasound was performed at 80 °C for 2 h, in order to fully mix the aminated carbon nanotubes and isocyanate and make them fully react; finally, the addition of polyurea component B (amino compound) is mechanically stirred evenly to prepare the coating. Three kinds of coatings of pure polyurea, 0.5 wt.% carbon nanotubes/polyurea and 1.0 wt.% carbon nanotubes/polyurea were prepared. The coating was prepared on the pretreated aluminum alloy substrate using an SZQ applicator. The average dry film thickness was $30 \pm 2 \mu\text{m}$ and the test was started after curing at the room temperature for 7 days.

2.2. Shore hardness and adhesion

The test was carried out by an LX-A Shore Rubber Hardness Tester. Hardness measurements were made on a polyurea block with a thickness of 10 mm. Ten points were randomly selected for measurement and averaged as the experimental results. The adhesion of the coating to the aluminum alloy substrate was tested using a PosiTest AT-M Coating Adhesion Tester.

2.3. Electrochemical impedance spectroscopy

The EIS test used the three-electrode system. The reference electrode is a Hg/HgO electrode and the auxiliary electrode is a platinum plate. The effective working area of the coating in the electrolytic cell is 19.625 cm² and the solution is 0.1 mol/L NaOH. The test was performed using the AutoLab PGSTAT 302N electrochemical workstation with a sinusoidal potential disturbance of 20 mV amplitude with a sweep frequency of 100 kHz to 10 mHz and the data was fitted by Zsimpwin.

3. RESULTS AND DISCUSSION

3.1. Hardness and adhesion

The Shore hardness A and the adhesion test results for the polyurea and the carbon nanotube-doped composite polyurea coatings on the aluminum alloy substrate are shown in Table 1.

Table 1. Shore hardness A and adhesion of carbon nanotubes/polyurea composite coatings

CNT (wt.%)	0%	0.5%	1.0%
Shore hardness A	48.5	70.3	78.8
Adhesion	6.82	7.13	7.26

The Shore hardness test results showed that the surface hardness of the coating increased with increasing CNTs addition. Hardness can provide a measure of the ability of a coating to resist deformation when pressed and may also reflect the bonding strength and cohesive ability. According to the hardness value, the uniformity and curing degree of the coating can be judged [15-16]. After the nanoparticles are added to the organic coating, the polymer segments will have three states [17] as shown in Fig. 1: the segments are cut through the particles; the segments are wound around the particles; the segments are wound around the particles and are brought closer together. All three states could enhance the cross-linking of the organic coating, reduce internal defects and improve its performance. When an external force acts on the surface of the polyurea coating, the polymer segment will continuously transmit the impact and exhibit better elasticity. When CNTs are added to the coating, the nanoparticles or agglomerated nanoparticles will hinder the polymer segment [18]. Adding CNTs to the elastomer will significantly improve the mechanical properties of the composite. This enhancement is not due to the

creation of strong interfacial interactions, but the large aspect ratio and physical entanglement with elastomer molecules of CNTs. Furthermore, the hydroxy CNTs can form a chemical bond with the isocyanate in the polyurea facilitating energy absorption, so that the strength and hardness of the material are further improved.

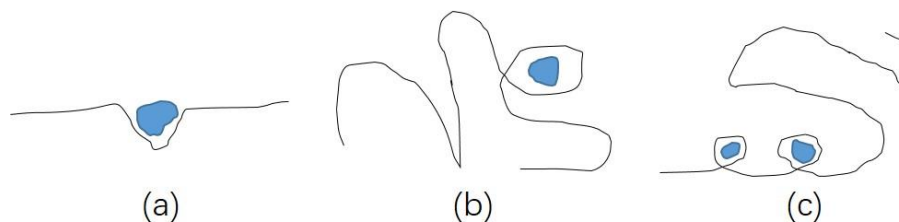


Figure 1. Polymer segment motion (a) the segments are cut through the particles (b) the segments are wound around the particles (c) the segments are wound around the particles and are brought closer together

The results given in Fig. 1 also showed that the adhesion of the coating to the aluminum alloy substrate was slightly improved after the doping, but the effect was not significant. The adhesion of the organic coating to the substrate is mainly related to the cohesive force of the organic coating itself and the adhesion of the coating to the substrate [19]. For polyurea coatings, when the NCO content is high, the urea bond and the urethane bonding in the primary chain is reduced [20]. At this time, fewer hydrogen bonds are formed between the coating and the substrate, so the hardness and adhesion of the polyurea are lower. The phenomenon of the enhanced adhesion may be due to the increased degree of cross-linking inside the coating and the reduction of internal defects after doping the CNTs. The adhesion of the coating under wet conditions is important for the protection of the substrate. The coating with good adhesion tends to have better shielding effect and its peeling resistance is also improved. Studies have shown that the anode area of the adhesive coating is much smaller than that of the non-adhesive coating [21].

3.2. Characteristics of EIS during immersion

The EIS results of the three coatings immersed in the 0.1 mol/L NaOH solution for 21 days are shown in Fig. 2.

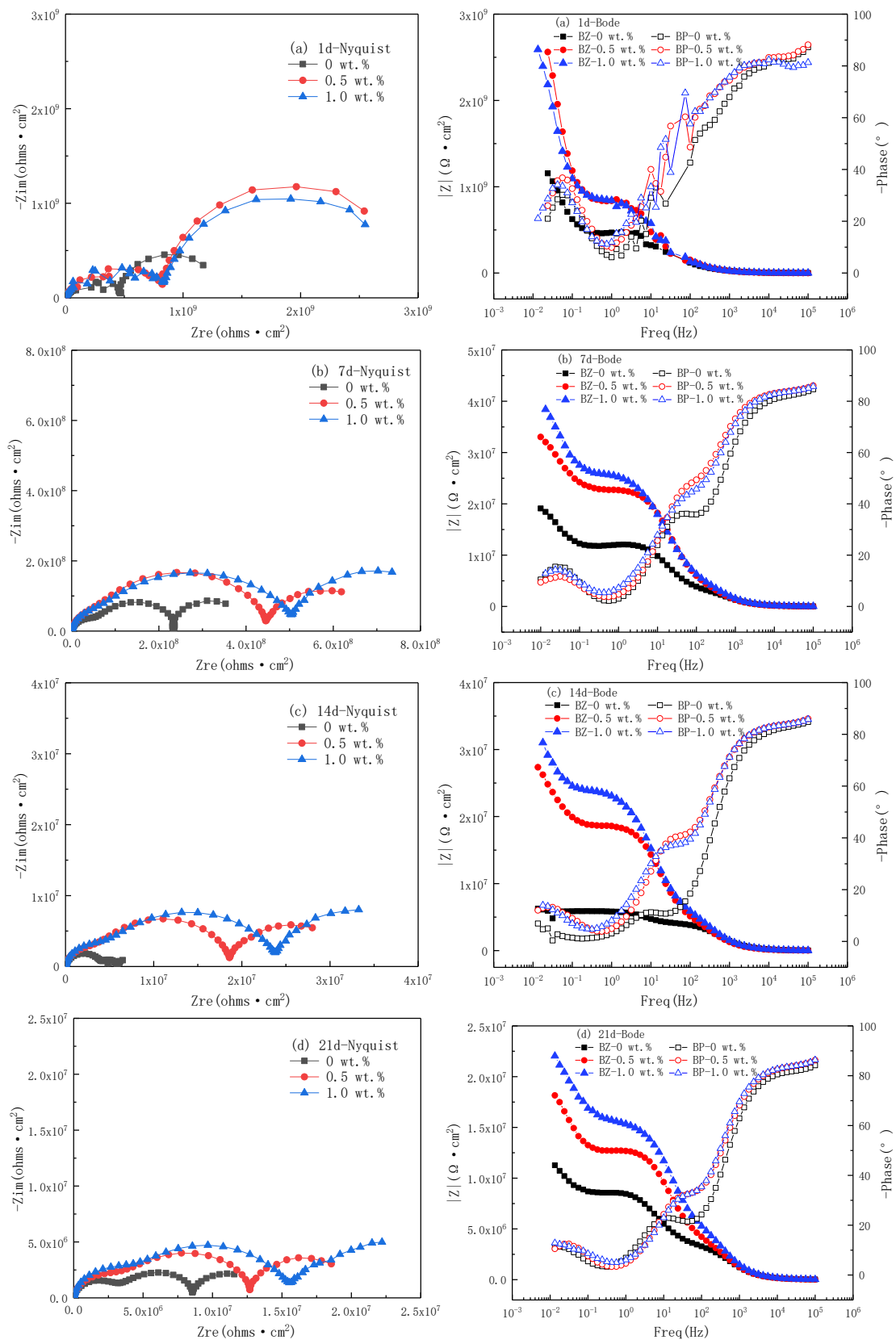


Figure 2. Nyquist plot and Bode plot of EIS during immersion process (a)1h(b)7h(c)14h

After soaking for 1 day, the Nyquist plot of the coating showed two arcs. At this point, water, air and aggressive ions in the solution had begun to enter the coating's micropores [22] and the coating could not completely shield the foreign matter from attack. The coating is only about 30 μm in this test, the normal construction thickness is in the millimeter range and even up to several centimeters depending on the construction requirements [23]. Therefore, the solution can rapidly react electrochemically with the substrate through the fewer micropores of the coating. Because there are fewer corrosion products at this time, there was a double-capacity arc in the Nyquist plot.

After soaking for 7 days, the Nyquist plot of the coating showed three inconspicuous arcs, indicating that there were three time constants. This may be due to the presence of a large number of micropores inside the coating; as more solution reacts electrochemically with the aluminum alloy substrate through the micropores of the coating, the corrosion products accumulate to form the third arc. Studies [24-25] have also shown that at this time, many of aggressive ions have reached the coating/substrate interface and reacted with the aluminum alloy to form a corrosion product film. Due to the presence of the surface oxide film, the Nyquist plot presents three capacitive reactance arcs.

After immersion for 14 days, the Nyquist plot of the coating still showed three arcs. The modulus in Bode plot continued to decrease but remained at the same order of magnitude as that on Day 7. The angle in Bode plot changed a lot at the low frequency, which may be caused by the dissolution and thinning of the surface oxide film, and the degree of corrosion was further aggravated. The Bode plot of the pure polyurea coating exhibited a lower resistance platform at low frequencies and there was no apparent third arc in the Nyquist plot. It is possible that the corrosion products accumulated in the micropores disappear, so that a large amount of corrosive medium and water are more easily contacted with the substrate through the micropores, resulting in a significant decrease in the protective ability of the coating during this period.

After soaking for 21 days, the Nyquist plot of the coating still showed three arcs. The modulus and amplitude variation of the three coatings shown on the Bode plot were similar. After immersion for a long time, the number of micropores inside the coating may have increased and the electrochemical reaction area will be larger resulting the reducing of the impedance modulus. The angle at the low frequency had changed significantly compared with the data of Day 1.

3.3. Equivalent circuit and fitting results

The equivalent capacitance of the coating can reflect water absorption of the coating and can be used to study the relationship between microstructure and coating failure [26,27]. The equivalent resistance of the coating is related to the size and number of the coating's micropores. Ions, water and oxygen can contact the substrate through the micropores and the porosity, and the shielding ability to solution of the coating can be measured by the change of the equivalent resistance [28,29]. The equivalent circuit is shown in Fig. 3. C_c is the coating equivalent capacitance, R_c is the coating equivalent resistance, C_{out} is the corrosion product equivalent capacitance, R_{out} is the corrosion product equivalent resistance, C_{dl} is the electric double-layer capacitance, and R_{ct} is the charge transfer resistance.

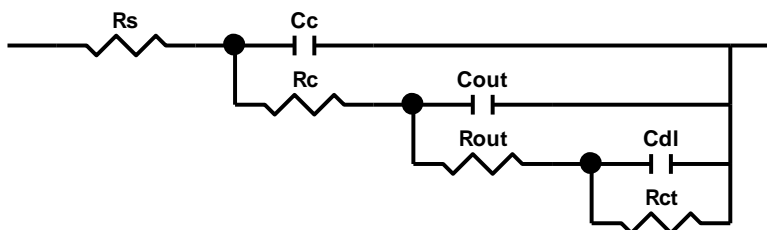
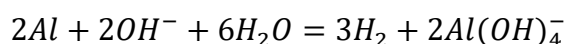


Figure 3. Equivalent circuit

Table 2 shows the EIS fitting results of this system during immersion. During the immersion period, the coating equivalent resistance of different coatings basically increased continuously, and the coating equivalent resistance basically continued to decrease, indicating that the coating constantly absorbed water and the shielding effect of coating on solution reduced. In alkaline solution, the oxide film of aluminum alloys lost its protective effect due to dissolution and hydrogen evolution reaction [30,31]. After the oxide film corroded, the substrate will react with the solution as follows:



After soaking for a long time, the coating absorbed more water, and the equivalent resistance of the corrosion product continued to decrease. When the coating was immersed in the solution, water absorption and ion transmission continued to occur, indicating that the corrosive medium continuously penetrated into the substrate, and the substrate/solution interface continued to expand.

Comparing the value of coating equivalent resistance (R_c) and charge transfer resistance (R_{ct}) during soaking, the CNTs doping amount of 0.5 wt.% and 1.0 wt.% had stronger barrier ability to solution than the pure polyurea coating. And the protective ability of the coating with the doping amount of 1.0 wt.% CNTs was better than 0.5 wt.% coating. However, the doping amount of 1.0 wt.% did not significantly improve the corrosion resistance of the polyurea coating, which may be due to the inert effect of CNTs, making it difficult to disperse in polyurea.

Table 2. Fitting results of EIS

CNT (wt.%)	Time (day)	C_c ($F \cdot cm^{-2}$)	R_c ($\Omega \cdot cm^2$)	C_{out} ($F \cdot cm^{-2}$)	R_{out} ($\Omega \cdot cm^2$)	C_{dl} ($F \cdot cm^{-2}$)	R_{ct} ($\Omega \cdot cm^2$)
0	1	4.488E-12	7.198E7	1.337E-11	3.635E8	4.381E-9	1.046E9
	7	9.185E-11	3.350E6	9.337E-10	8.395E6	7.992E-7	8.968E6
	14	7.542E-11	8.929E5	4.076E-11	2.820E6	2.289E-8	2.249E6
	21	8.386E-11	4.565E5	3.694E-11	2.304E6	1.660E-8	5.121E6
0.5	1	4.997E-12	1.280E8	1.534E-11	6.734E8	2.137E-9	2.495E10
	7	9.877E-11	5.338E6	3.990E-10	1.682E7	4.166E-7	1.126E7
	14	9.999E-11	4.798E6	6.394E-10	1.254E7	2.831E-7	3.171E7
	21	1.025E-10	4.065E6	1.173E-9	8.264E6	8.205E-7	7.028E6
1.0	1	5.094E-12	9.331E7	9.344E-12	6.748E8	2.319E-9	2.831E9
	7	8.462E-11	5.897E6	4.888E-10	1.845E7	3.066E-7	1.664E7
	14	8.602E-11	6.111E6	8.233E-10	1.674E7	5.390E-6	1.379E7
	21	8.762E-11	5.200E6	9.802E-10	9.933E6	5.668E-7	8.209E6

Combined with the effect of CNTs on the surface hardness and adhesion of polyurea coatings, the improvement in corrosion resistance indicated that the nano-sized particles can be effectively filled in the cross-linking network of polymer to enhance the compactness of the coating and could effectively shield water, air and corrosive media [32-33]. Furthermore, the hydroxy CNTs can react with the isocyanate in the polyurea to form the urethane bond, so that the degree of cross-linking of the material itself is enhanced and internal defects are reduced [34].

4. CONCLUSION

The surface hardness of polyurea coating increased after doping with CNTs. The adhesion on the aluminum alloy substrate was slightly enhanced, but the improvement was not so significant. When the CNTs were doped into the polyurea coating, the internal crosslinking degree of the polyurea was increased, the defects of the coating reduced and the internal density of the coating enhanced. Corrosion resistance can be obtained by comparing the characteristic changes and fitting results of EIS. The relationship between the doping amount of carbon nanotubes and corrosion resistance is $1.0 \text{ wt.}\% > 0.5 \text{ wt.}\% > 0 \text{ wt.}\%$.

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