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Preparation and Properties Study of Polyaniline Conductive Anti-Fouling Coatings

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An antifouling coating was prepared with the polyaniline(PANi) as conductive filler, chlorine ether resin as film forming material, and methylsulfonic acid as doping acid as well as other additives. The influences of PANi content on the coating's conductivity, physical properties and chemical resistant performance were studied. The electrochemical behavior of the electrode painted by the coating was investigated by Tafel analysis and electrochemical impedance spectroscopy measurements. Results showed conductive properties were significantly influenced by the mass ratio of doping acid/PANi, and when the mass ration of doped methylsulfonic acid/PANi was 1:1, surface resistance obtained a lowest value. Conductive properties, chemical substances resistance and anti-corrosion properties of conductive coatings were all affected by the concentration of PANi added: the concentration of PANi added in the coating should be controlled in the range from 15% to 25% range, where it had both perfect conductive property and unique corrosion property. Electrolysis tests showed that an electrode made by the conductive coating could produce a certain concentration of HOCl, so as to achieve the anti-fouling purpose.

Keywords: polyaniline; conductive coating; anticorrosion performance

1. INTRODUCTION

In order to prevent the formation of marine organism fouling, for decades there had been an upsurge of interest in the development of antifouling technology relying on some traditional antifouling toxins, such as cuprous oxide (Cu_2O) or tributyltin (TBT) [1], which were mixed into antifouling paints and slowly released to hinder the marine organism from attachment. These materials often have a short service life; besides, they might do harm to the marine environment [2,3,4]. To avoid the pollution, the development of new non-toxic antifouling methods were pursued [5] and a method called anti-fouling with electrolyzing seawater [6,7,8] was employed to generate HOCl solution which could prevent the emergence of fouling owing to the effect of HOCl.

How the conductive coating works is shown as followings: first, an insulating film is painted on the hull plate that might contact with sea water, and then another layer of conductive coating is coated. Here, the conductive coating serves as an anodic electrode, on which the sea water would be electrolyzed to generate HOCl if there is current going through it. Ultimately, a hypochloric acid film covering the conductive coating surface will hinder the marine organisms from adsorbing on the surface. Therefore, it is of great significance to develop a sustainable antifouling conductive coating.

The traditional conductive coating is often prepared by dispersing the conductive filler such as graphite, carbon black, metal powder or metal oxides into the organic or inorganic resin, which leads to a large consumption and an un-uniform distribution of conductive filler, a high cost and a poor quality of its conductive properties [9,10]. Fortunately, with the development and exploration of the conductive polymer materials, it is found that organic conductive polymers such as PANi, poly thiophene and pyrrole have excellent conductive properties, especially, when they are mixed with some doping acid, their conductivity performance could be as good as metal.

Among these, polyaniline (PANi), a conductive polymer material, has a unique doping properties and a perfect electrochemical reversibility[11,12,13,14] when it is mixed with doping acid and some nano-powder (carbon、TiO_2 and so on) . Compared with other polymer materials, the low price, simple synthesis process, unique conductive properties and high thermal stability make PANi one of the most potential conductive antifouling materials. It has been confirmed that PANi is the most promising conductive polymers and had become the focus of investigation and exploration [15,16,17].

In this paper, how to prepare the conductive coating is set as the basic thought. A series of different contents of PANi conductive coatings with additives were prepared, and their properties were carefully investigated in order to develop a conductive coating with the best conductive properties and suitable to electrochemical antifouling.

2. EXPERIMENTAL

2.1. Materials

PANi was purchased from Zhengji Company (Jilin, China). Chlorine ether resin MP25 was purchased from Jiangyin Huitong Fine Chemical Agent Company (Jiangsu, China). Methylsulfonic acid and dimethylbenzene were purchased from Shanghai Chemical Reagent Company. Nanometer titanium dioxide was purchased from Iron and Steel Institute of Panzhihua (Sichuan, China). Titanate coupling agent was purchased from Nanjing Capture Chemical Company (China). Defoamer5300 and Dispersant were purchased from Deuchem (Shanghai, China). Sodium chloride, Sodium hydroxide and Sulfuric acid were purchased from Chongqing Beibei Chemical Reagent Plant (China). All solutions in this study were prepared in distilled water.

2.2. Conductive coating preparation

Figure 1 showed the process of preparing the conductive coating. Firstly, put PANi, methylsulfonic acid, nanometer titanium dioxide as well as some mixture of titanate coupling agent and dimethylbenzene into a JHS-1 model electronic blender (Hangzhou Meter Motor Factory); then made the blender work at a constant speed of 1400r/min for 12 hours, and at the same time, mixed the chlorinated polyether resin and dimethylbenzene to have the chlorinated polyether resin solved enough; next, mixed the PANi mixture with the chlorinated polyether resin mixture and grinded them twice with a grinding miller at a low speed with a QMZ-1 Grinder (Tianjin Material Testing Machine Plant). Then, an ultrasonic process should be done in a SK7200LH Ultrasonic instrument (Shanghai Kudos) at least for an hour. Finally, another resin needed to be added and a high speed blundering process (1400r/min) should be carried out for 12 hours. Some solvent were added to adjust the viscosity and the conductive coating could be obtained.

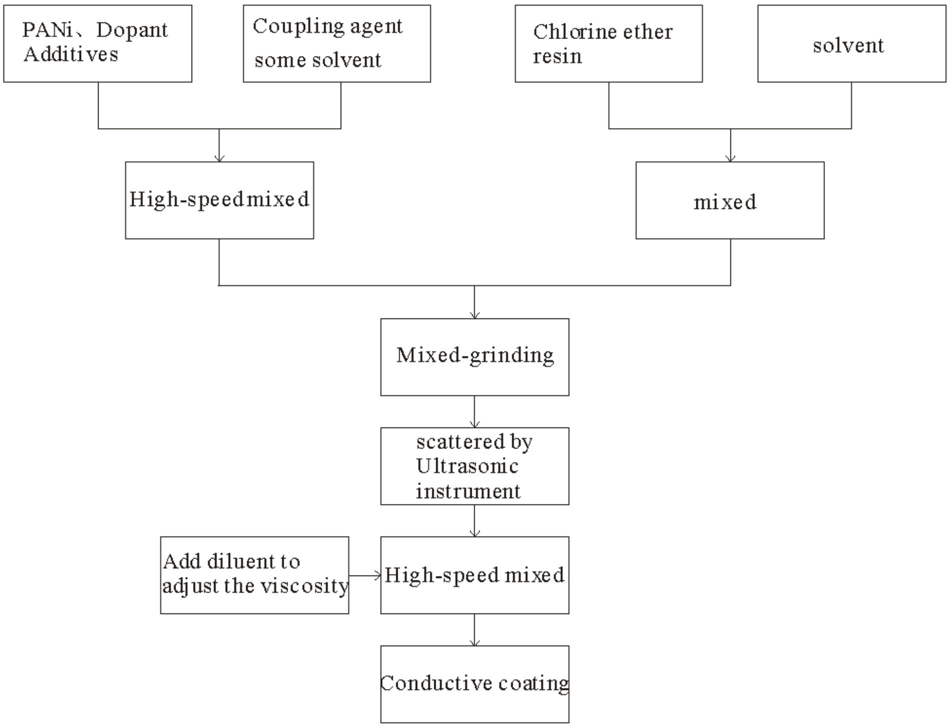


Figure 1. Process of making coating

2.3. Performance test of the conductive coating

Performance testing of acid, alkali and salt

The steel plates (Bought from China National Center for Quality Supervision & Test of Coating) used for the acid alkali salt tests have a dimension of 150mm×70mm×0.5mm. Before painting the conductive coating, the steel plate should be de-greased by a soaking process in a certain amount of alkaline solution, washed with clean water and roughed via a tiny corrosion process with acid to enhance its adhesion to the coating, then immersed in acetone and ethanol, cleaned with stilled water and dried with hot air. After that, painted the conductive coating of different PANi amounts evenly on the steel plate with a wolf hair brush and when the conductive coating was solidified, put it in an acid solution (5%H_2SO_4), an alkaline solution(5%NaOH) and a salt solution (3.5%NaCl) respectively. The measurements could be performed in the three types of solutions.

2.4. Anti-corrosion performance test

Electrodes preparation

The working electrodes used for electrochemical measurements were prepared by A3 steel, which had poor anti-corrosion properties. The protection behavior of the coating could be investigated by the use of A3 steel as the electrode.

The working electrodes (4mm×Φ20mm) were prepared by linking a 10cm copper wire to its bottom surface and embedded in an epoxy resin, just leaving the top surface as the working area. Then they should be abraded gradually with emery paper 400、600、800、1000＃ to get a mirror-like surface, ultrasonically cleaned with acetone and ethanol to remove the organic impurities and dried with cold and hot air. Finally, painted the working area with the conductive coating and dried it in a ventilating place for 7 days and the tests could be conducted when it was totally solidified.

Tafel polarization curves measurements

The *Tafel* polarization cures were measured by a PGSTAT302 *Autolab* electrochemical measurements system (Metrohm Autolab), which were used to test the effect of the conductive coating on the corrosion behavior of the electrodes. The potential scan was started from -250 mV to +250mV versus the open circuit potential with a scan rate of 1 mV/s. The corrosion rate was determined according to the anodic current density. During the measurements, a NaCl solution (3.5% w/w) was used as the corrosion medium, a saturated calomel electrode as the reference electrode and a platinum plate as the auxiliary electrode. The working electrode was achieved by applying a conductive coating to the surface of the previous A3 steel. The equipment for polarization curves tests is shown in Figure 2.

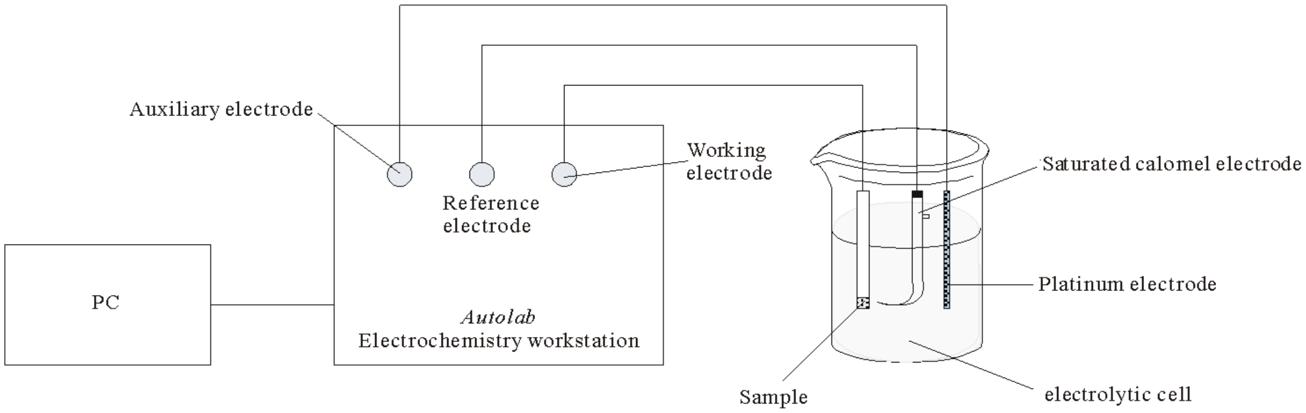


Figure 2. The electrochemistry test equipment

Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy tests were performed in the *Autolab* electrochemical measurements system in the frequency range of 100 kHz to 10 MHz with an amplitude signal of 5 mV, which were similar to the polarization curves measurements. It was conducted according to the following sequence：

i.) Filled 2/3 of the electrolytic cell with the 3.5%NaCl solution, and connected the working electrode, the calomel electrode and the platinum electrode with the Autolab electrochemical measurements system and checked the corrosion potential of the working electrode;

ii.) 30 min later, when the corrosion potential reached a stable state, the electrochemical impedance spectroscopy measurement could be carried out.

2.5. Comprehensive evaluation of the conductive coatings

According to the previous experimental data and the investigation results, the conductive coatings were prepared by a certain amount of PANi as well as other materials, and their morphologies were analyzed by XDS-1B inverted microscope (Chongqing Optical Instrument Factory) and Benyuan CSPM5000 Atomic force microscope(Benyuan Co., China).

Observation of conductive coatings morphologies: firstly, painted each prepared conductive coating on the glass slide, observed its morphology through the inverted microscope (magnified to 100 times) and then the morphology analysis was conducted in the mode of atomic force microscope with the apparatus parameters set as followings: scanner:S2037; resolution: 512×512; and scan frequency: 2.0Hz.

3. RESULTS AND DISCUSSION

3.1. The influence of the doping acid amounts on the surface resistance of the conductive coating

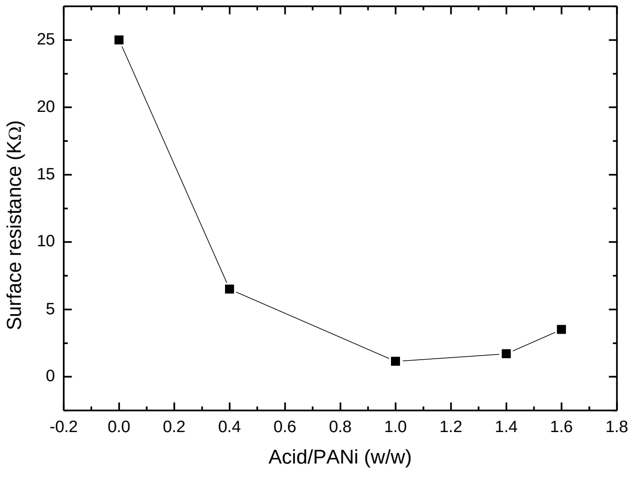


Figure 3. The relationship between the surface resistance and the weight ratio of methysulfonic acid/PANi

Figure 3 showed the surface resistance of the doped PANi which was achieved by keeping the PANi amount constant and adjusting the mass ratio of methylsulfonic acid/PANi in the range from 0.0 to 2.0.

It was clear that the surface resistance decreased with the increasing concentration of methylsulfonic acid, however, when the mol ratio of methylsulfonic acid/PANi reached 1.0, the surface resistance began to increase. This was ascribed to the fact that at a low methylsulfonic acid concentration, the doped ratio of the PANi was small and the possibility of forming a conductive channel was low, which led to a large surface resistance. However, when the doping rate was saturated, an increase addition of methylsulfonic acid would not be helpful to the increase of the conductivity of the coating due to the fact that the excess methylsulfonic acid left in the products would be partly precipitated during the drying process, and the other methylsulfonic acid, residual in the products, however, had no effect on promote the inductivity of the coating due to its insulative properties and conversely, it blocked the conductive channel formed by the large PANi molecules which finally caused an increase in the surface resistance. Therefore, the mol ratio (methylsulfonic acid/PANi) was important for the conductive coating preparation. In order to obtain a conductive coating with low surface resistance, it was necessary to choose a proper mol ratio of methylsulfonic acid/PANi.

In addition, Figure 3 showed that when the mass ratio of methylsulfonic acid/PANi was 1.0, the best doping property was obtained and the coating applied in the latter research would all be prepared with such a ratio of methylsulfonic acid/PANi.

(a)appropriate doping (b)excessive doping (c)more excessive doping

Figure 4. The comparison schematic diagram of adding excess doping acid

3.2. The influence of PANi concentration on the conductive coating properties

With the mass ratio of methylsulfonic acid/PANi set as 1:1, six types of conductive coatings were prepared by adjusting the PANi concentration (10%, 15%, 20%, 25%, 30%, and 40% by weight) added in the film. The surface resistances of the six conductive coatings were shown in Figure 5.

In Figure 5, the surface resistance decreased linearly with the increasing PANi concentration when its concentration (by weight) was ranged from 10% to 20%. But with the increase of PANi content, the surface resistance decreasing tendency became smaller and gradually reached a stable value. This is due to the fact that at a low PANi concentration, the distance between the conductive particles is large, and a few PANi molecules could link with each other to form a chain-like conductive channel and the surface resistance is largely decreased. When the concentration reached 20%, the conductive channel has already been formed, and adding more PANi will not lead to an increase in the formation of the conductive channels, thus, the decreasing tendency of the surface resistance is gradually reduced and it finally reaches a stable value.

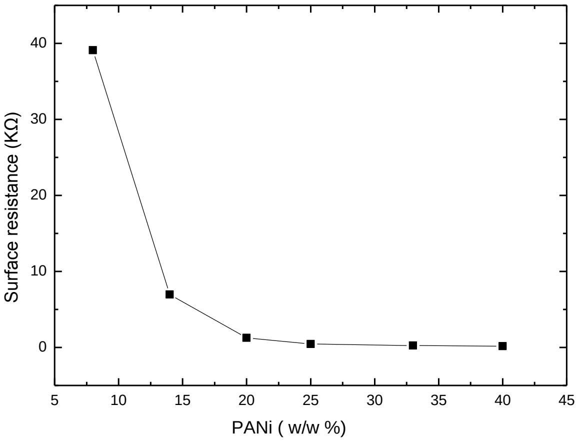


Figure 5. Influence of PANi content on surface resistance

3.3. The influence of PANi concentration on the chemical resistant of the conductive coating

The metals with a conductive coating is usually on the passive state due to the fact that a condense oxide layer is formed on the metal/PANi interface to protect the metal from corrosion. With a unique scratch and pitting corrosion resistance properties, PANi could be widely applied as an advanced anti-corrosion coating in the industry and even in some severe conditions. The oxide layer called the passive film could protect the underneath iron from further corrosion. It was reported by related articles[18] that an electric field opposite to the electronic transfer direction is formed between the metal surface and the PANi surface, which works as a charge transfer barrier layer, hindering the electrons transferring from the metal to the oxides.

Table 1 listed the experimental data of the conductive coatings with various concentration of PANi after 48 hours' immersion in the acid solution, alkaline solution and sea water respectively. The results indicated that the anti-corrosion properties of the conductive coatings decreased with the increasing concentration of PANi. When the PANi concentration was lower than 20%, the coating showed no differences after 48 hours' immersion and exhibited a perfect chemical resistance property. Nevertheless, when the PANi concentration was higher than 25%, bubbles appeared in the coating, which might be a result of a reduction of its compactness owing to the high concentration of PANi. It was said that an increase of the PANi concentration in the coating would lead to an increase of the coating surface roughness and a decrease of its compactness, which caused a poor effect, namely, the medium permeating speed into the coating was too high and the formation speed of the passive film was lower than its dissolving speed, thus, the passive film formed on the metal surface was dissolved by the corrosion medium and corrosion was induced whereas the hydrogen generated in the cathodic reaction led to the appearing of bubbles. Meanwhile, the results also suggested that the chlorinated polyether resin was served as a carrier and supported in the conductive coating. Due to the fact that PANi could not form a firm connection with metals, its concentration should not be too high and with the cost taken into account, PANi added in the coating should be less than 25%.

Table 1. Effect of PANi content on chemical medium resistance of coatings

Sample(PANi%)	NaCl (3.5%)	NaOH (5%)	H2SO4(5%)
1 (10%)	No change	No change	No change
2 (15%)	No change	No change	No change
3 (20%)	No change	No change	No change
4 (25%)	Microbubbles	A few small bubbles	A few small bubbles
5 (30%)	Microbubbles	Massive bubbles	Massive bubbles
6 (40%)	A few small bubbles	Massive bubbles	Massive bubbles

3.4. Electrochemical testing of the PANi coating corrosion resistance

Tafel polarization curves measurements of the coatings with various concentration of PANi

Four types of conductive coatings identified by different additions of PANi, i.e., 15%, 25%, 30% and 40% were prepared and they were painted on the working electrodes made by A3 steel. *Tafel* polarization curves were measured on these electrodes in 3.5% NaCl solution and the results were plotted on Figure 6 (*a, b, c* and *d*). The corrosion potentials and the corrosion current densities could be obtained by extrapolation of the *Tafel* zone in the polarization curves. Comparing the *Tafel* curves of a, b, c and d with that obtained on the A3 steel electrode without any coating, we could find that the corrosion potentials of the A3 steel had a large positive shift and the corrosion current densities were remarkably decreased in the presence of PANi. For the coating with the PANi concentration of 15%, 25% and 30%, the corrosion potentials shifted to the positive direction as large as 0.777V, 0.830V, and 0.927V respectively, and the corrosion current densities were decreased by 2 to 3 orders of magnitude. It was reported that the more positive corrosion potential the metal had, the more stable the metal was, and the smaller its corrosion possibility was at its service potential, which was due to the fact that the conductive coating had protected the metal, suggesting that the conductive coatings had a remarkable anti-corrosion effect on the metal matrix. When the concentration of PANi reached 40%, however, the corrosion potential began to decrease and the corrosion current density began to increase. This indicated that the increasing amount of PANi led to the decrease of the conductivity of the coating and the barrier effect of the electrons transfer; meanwhile it increased the surface roughness, which increased the micro defects largely and the medium permeating speed. As a result, the anti-corrosion effect of the coating was decreased.

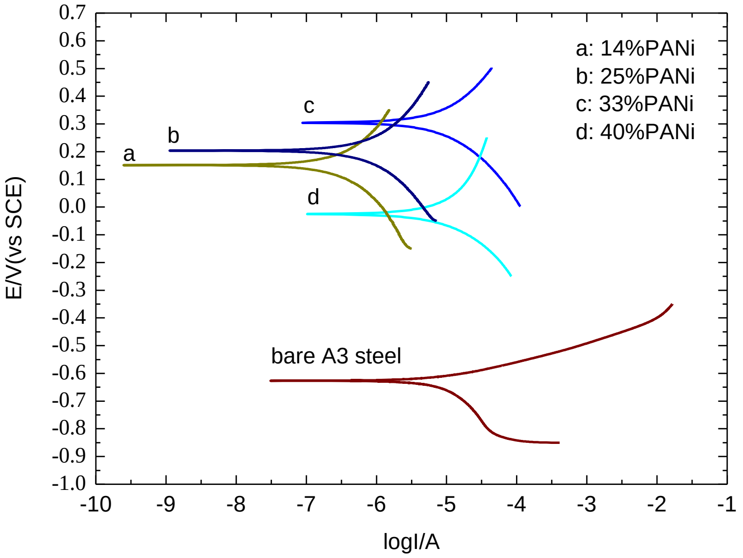


Figure 6. *Tafel* curves of film containing different PANi in NaCl solution (3.5% w/w)

Electrochemical impedance spectroscopy (EIS) measurements of the conductive coatings with various concentrations of PANi

Figure 7 and Figure 8 displayed the EIS results of the samples without (bare A3 steel) and with various PANi concentrations (15%(a), 25%(b), 30%(c), and 40%(d)) of PANi.

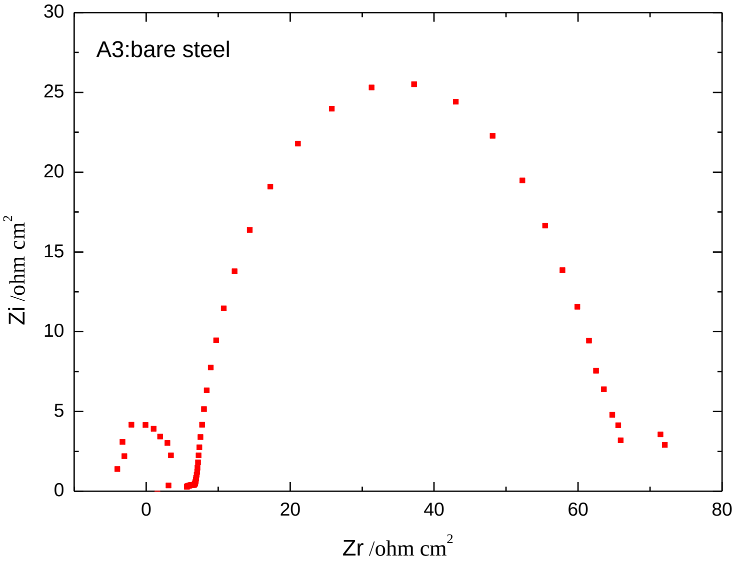


Figure 7. Nyquist diagram for A3 steel in NaCl solution (3.5% w/w)

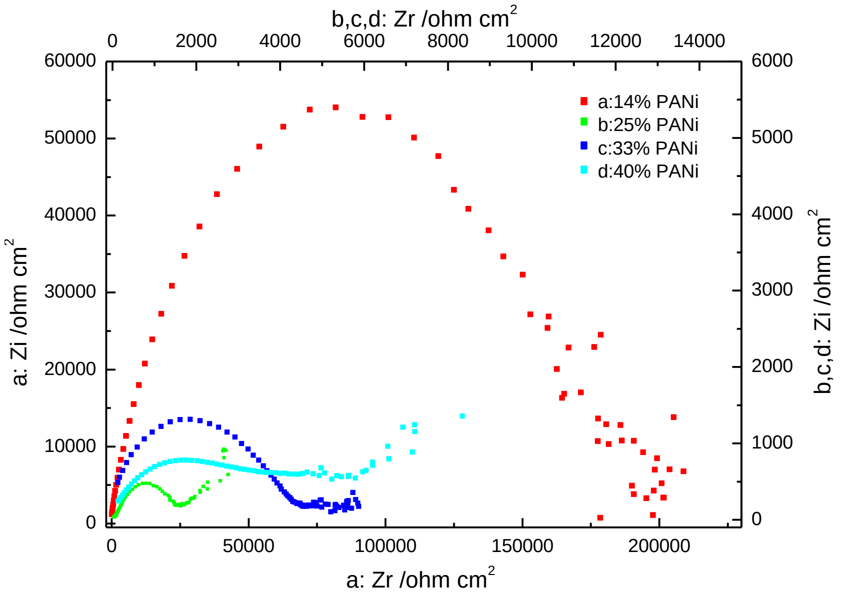


Figure 8. Nyquist diagrams for film containing different PANi in NaCl solution (3.5% w/w)

The impedance value is an important parameter to evaluate the anti-corrosion effect of the coating in a long time, which directly reflects the permeating ability of the corrosion medium into the coating [19]. The larger the impedance value is, the more time the corrosion medium takes to pass the coating and the better the anti-corrosion properties of the coating is. Seen from Figure 4, it was clear that the impedance of the samples covered by the coating with PANi was higher than the bare A3 steel sample, which indicated that the conductive coatings had a remarkable corrosion inhibition effect for A3 steel.

The *EIS* data were fitted by the *Autolab* software and from the fitting results, the charge transfer resistance of the bare A3 steel electrode was only 52Ωcm^2. In Figure 8, as to the curves of *b, c*, and *d*, there was a semicircle appearing in the high frequency range and a line characteristics of *Warburg* impendency appearing in the low frequency, which was ascribed to the fact that the PANi particles in the coating had a large barrier effect, corrosion could only occur at the interface of the metal matrix and the corrosion medium which reached there by a penetration process through the particles pores, thus, the corrosion process of the metal matrix mainly depended on the mass transfer process and the electrochemical reactions. Curve *a* in Figure 8 had only a semicircle, indicative of only one time constant and the impendence of the related coating was about 161 kΩcm^2, which was much larger than that of *b, c* and *d* (about 1~4kΩcm^2), suggesting the corrosion process was controlled by the electrochemical reaction, namely, the conductive coatings could effectively hinder corrosion medium from penetrating into the metal surface. These results were in good agreements with the *Tafel* curves analysis, implying that the conductive coatings had unique anti-corrosion properties and excess of PANi particles would lead to an increase of coating surface roughness and a decrease of the coating tightness which finally resulted in the corrosion medium penetrating to the metal/coating interface and initial of corrosion.

The measurements results suggested that the anti-corrosion properties of the conductive coating decreased with the increasing concentration of PANi. Thus, the amount of PANi added in the coating should not be too high, and an addition of 14～25% would be suitable, at which the coating could obtain both a unique conductive properties and a best anti-corrosion characteristics.

3.5. Coatings morphology observation

With PANi as the conductive materials, chlorinated polyether resin as the film formers as well as some other additives, the conductive coatings were prepared. Figure 9 displayed microscope images (100×) of these coatings tested by painting on the glass slide surface. It could be seen that the size of the solid particles in the conductive coatings were small, indicating PANi particles had dispersed uniformly in chlorinated polyether resin. The PANi particles were fibrous and connected to others, forming a charge transfer net.

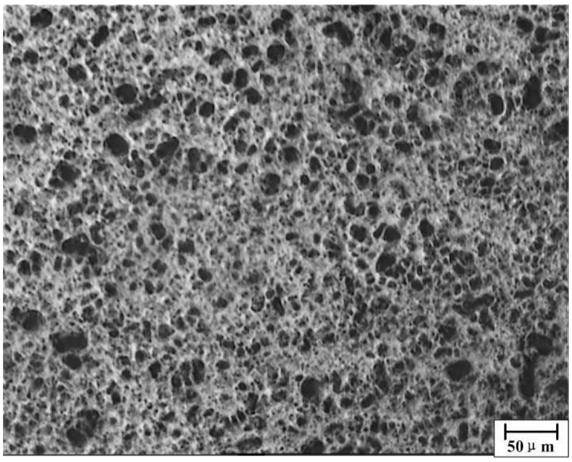
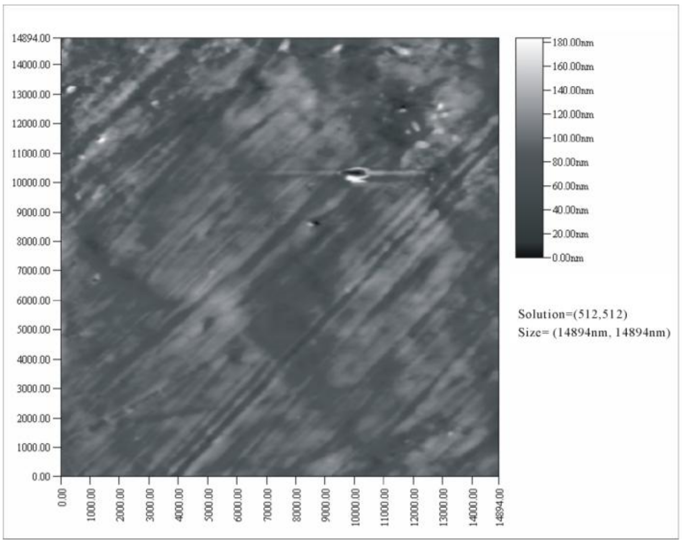


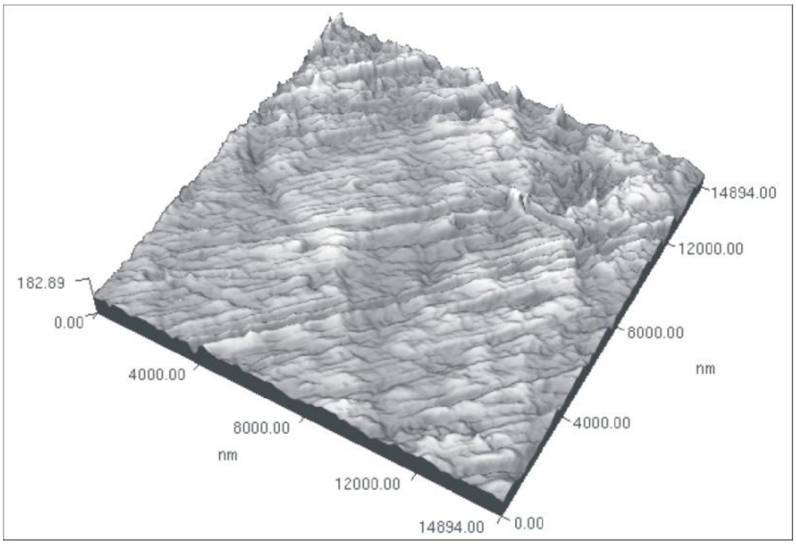
Figure 9. The photo of conductive coating by using microscope at 100×

Figure 10 showed the optical and AFM images of the coatings surface morphologies. From the optical images, the coatings surfaces were not rough but smooth. Due to the fact that AFM image was obtained by measuring the interaction of the samples with a special probe, its resolution was at the atomic level. From the two-dimension and three-dimension maps in Figure 10, the micro surface of the conductive coating was condensed and the coating was continuous with a large area. The roughness of the coating surface (*Ra*) was only 11nm and its surface heights distribution was shown in Figure 11. It could be observed that the heights followed a normal distribution with the average height of 91nm, indicating the surface of the prepared coating was very smooth. The particles in the conductive coating were assigned to PANi molecules, the particle size of which had a large distribution range. As shown in Figure 11, the average particle size was 249 nm, indicating PANi molecules were small and could be easily connected with others to form a conductive network.

(a) visual two-dimensional surface



(b) two-dimensional surface measured by AFM



(c) three-dimensional illustration measured by AFM

Figure 10. The surface of conductive coating

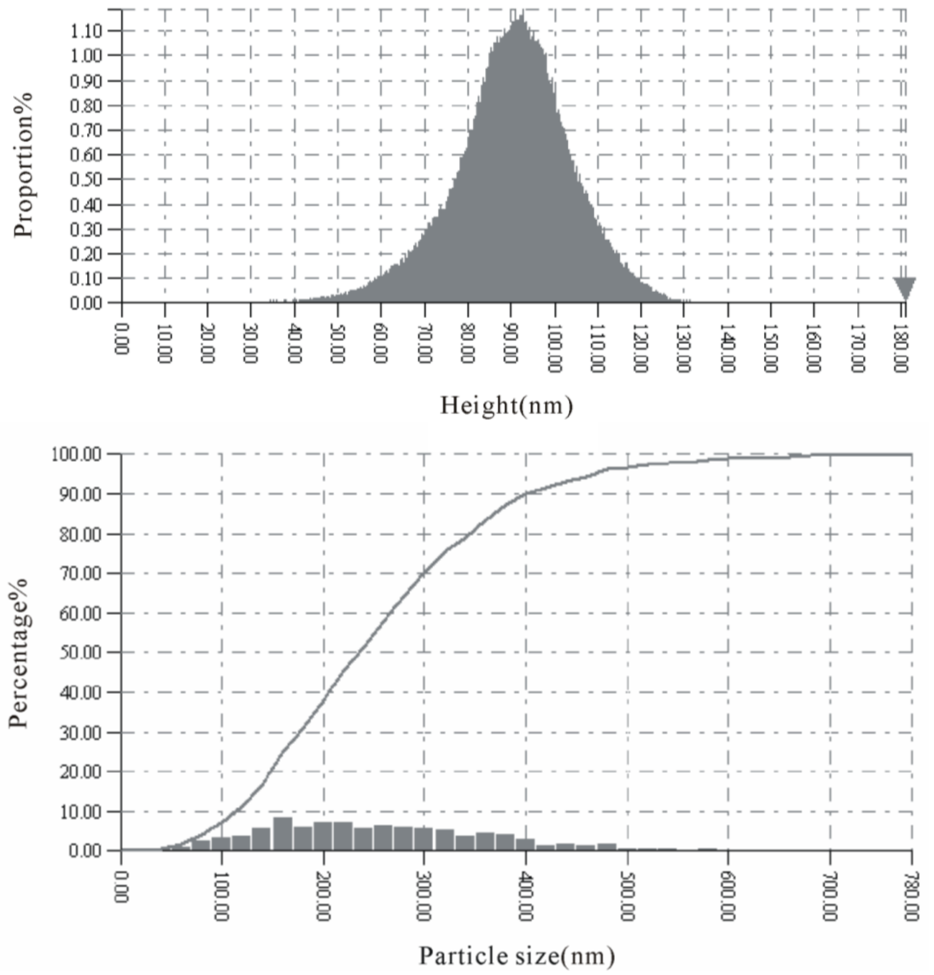


Figure 11. The distribution map of conductive coating's surface height and conductive coating's particle size

3.6. Concentration of HClO in test solution

As previous mentioned, in order to obtain a better conductive coating, we produced a conductive coating with 15% PANi and the weight ratio of methysulfonic Acid/PANi as 1/1 to prepared the electrode for electrolysis. We designed a simple system to produce HOCl, which was mainly made up of a potentiostat and a self-made working electrode (painted by PANi conductive coating). We measured the concentration of HOCl in 3.5 wt % NaCl solution (100 ml volume) by HClO Rapid Tester (Type S-CL501,QingShiJie Technology Co., Ltd, Shenzhen). As the instrument range limits was (0-2mg/L), the HOCl concentrations were measured under a lower current density and electrolysis time and the data were showed in Table 2. When the current density was low (1mA/cm^2), the concentrations of HOCl were not observed to be significant with increasing electrolysis time. While the current density increased, the concentrations of HOCl were observed to be notable with increasing electrolysis time. At the same electrolysis time, the concentrations of HOCl were observed to be notable with the current density raised. From the table we could find that in order to obtain a higher HOCl concentration, the electrolysis time and current density should be greater than 2 minutes and 10mA/cm^2 or 4 minutes and 5mA/cm^2. If the HOCl concentration is greater than 0.1~0.30mg/L[20], and this will effectively prevent adsorption of microorganism's, thus achieves the antifouling purpose.

Table 2. Concentration of HOCl under different electrolysis time and current density

Time	Current Density			
	1A/cm2	5A/cm2	10A/cm2	15A/cm2
2mins	0.01mg/L	0.02mg/L	0.54mg/L	0.64mg/L
4mins	0.02mg/L	0.77mg/L	1.38mg/L	1.78 g/L
6mins	0.03mg/L	1.41mg/L	-	-
8mins	0.05mg/L	-	-	-

4. CONCLUSIONS

A new type of conductive coating was prepared by the conductive polymer PANi (the filler), chlorinated polyether resin (the film formed material) and other addictives. The experimental results illustrated that:

(1) The surface resistance of the conductive coating was significantly influenced by the mass ratio of doping acid and PANi and when the mass ration of doped methylsulfonic acid/PANi was 1:1, the surface resistance obtained a lowest value.

(2)The conductive properties, chemical substances resistance and anti-corrosion properties of the conductive coatings were all affected by the concentration of PANi added: when the concentration of PANi was higher than 15%, the coating got perfect conductive properties and when it was lower than 20%, the coating had a high chemical resistance. The *Tafel* polarization cures investigations and *EIS* measurements suggested that when the concentration of PANi was in the range from 15% to 25%, the conductive coating had unique anti-corrosion property. Based on the tests results and in account of the performance price ratio, the concentration of PANi added in the coating should be controlled in the 15% to 25% range, where it had both perfect conductive property and unique corrosion property.

(3) Electrolysis tests showed that an electrode made by the conductive coating could produce a certain concentration of HOCl, which could be greater than 0.30mg/L, so as to achieve the anti-fouling purpose.

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