Study on preparation of amphiphilic silane and its modification on copper surface

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Abstract. The amphiphilic polymers monosilane and disilane were synthesized in this study. The pretreated copper plates were modified by the synthesized silane. The copper plates after silane treatment were characterized by measuring total reflection fourier infrared spectroscopy (ATR-FTIR), electrochemical impedance, X-ray photoelectron spectroscopy, and contact angle. ATR-FTIR and XPS confirmed that the amphiphilic polymer silane was successfully grafted onto copper surfaces; the contact angle measurement results showed that the contact angle of the surface of the copper plate after grafting the silane was reduced from 83° to 50°; the electrochemical impedance results showed that the electrochemical transfer resistance on the surface of the copper plates after grafting the silane was increased from 702.8 to 6452.

1. Introduction
A large number of studies[1-7] have shown that the corrosion resistance of metals can be enhanced after the metal surface is modified by amphiphilic polymer which containing polyethylene glycol segments. Amphiphilic polymer has the advantages of polymer viscosity and low molecular surface activity. Amphiphilic polymer has the affinity to both water and oil, so it has many unique physical and chemical properties.

K. Kamburova researched the preparation of stable aqueous suspension of positively charged colloidal PANI-SiO$_2$ particles suitable for electrodeposition with zinc on cathode (steel) surface. The PANI-SiO$_2$ particles were incorporated into the zinc coating by co-deposition of the particles and zinc from zinc sulfate electrolyte solution. The surface morphology of the hybrid zinc coatings was investigated by recording the SEM images before and after treatment in a model corrosion medium (5% NaCl solution with pH 6.7). The electrochemical tests revealed higher resistance of the hybrid coating to corrosion compared to the ordinary zinc coating[8].

Amphiphilic polymers have become the intersections of chemistry, chemical engineering, petroleum, medicine, materials, physics, electronics and life sciences, and the study of amphiphilic polymers has been one of the research hotspots in the field of polymer materials [9].

2. Experimental

2.1. Materials
Polyethylene glycol monomethyl ether (chemically pure), 2,4-toluene diisocyanate(chemically pure), polyethylene glycol(chemically pure) were purchased from Wuhan Jiangbei Chemical Reagent Co., Ltd., Wuhan, China; acetic acid (analytical grade) ,KH560 (analytical grade) were purchased from
Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China; polyetheramine (chemically pure) was purchased from Tianjin Xingyue Chemical Co., Ltd., Tianjin, China; acetone (analytical grade) was purchased from Tianjin Tianli Chemical Co., Ltd., Tianjin, China; copper plate (type H32) was purchased from Tianjin Xiwang Co., Ltd., China.

2.2. Synthesis of amphiphilic polymer silane
0.2 mol 2,4-toluene diisocyanate, 0.2 mol polyethylene glycol monomethyl ether and acetone were added in a 500ml three-neck flask which was equipped with a stirrer, a condenser, and a dropping funnel. The mixed solution was stirred at 60°C for 2h. The progress of the reaction was monitored by measuring the -NCO content through the di-n-butylamine method[10]. When the -NCO content was close to the theoretical value, the prepolymer was obtained.

0.2mol polyetheramine was added in another 500ml three-neck flask which was equipped with a stirrer, a condenser, and a dropping funnel. The above prepolymer was added dropwise into the equipment and the mixed solution was stirred at 60°C for 2h. As the NCO characteristic peak disappeared detected by infrared spectroscopy, then gradually added dropwise 0.2 mol or 0.4 mol KH560 through the dropping funnel. The reaction continued for a period of time, when the epoxy group characteristic peak disappeared detected by the infrared spectroscopy, the solvent was extracted under reduced pressure to obtain the products, which were the amphiphilic polymer monosilane and the disilane.

2.3. Pretreatment of metal surfaces and modification of metal surface with silane
Copper plates surface pretreatment and modification: The experimental size 20mm × 20mm brass (H62) was polished with 500 and 1000 grit sandpaper, respectively, and then degreased by ultrasonic cleaning with acetone. Then the degreased copper plates were immersed in a mixed solution of 2.5mol/L NaOH and 0.1mol/L ammonium persulfate for 60 minutes. After being taken out, the plates were washed with deionized water and ethanol in order, and then dried in cold N2, and then dried in an 80°C oven for 30 minutes.

5% (w / V) silane ethanol -water (90 / 10) solution was prepared well. The pH value of the solution was adjusted to 4-5 with acetic acid, and the solution was stirred with magnetic stirrer for 24 hours. The pretreated copper plates were soaked in room temperature for 2 hours. The copper plates modified by pretreatment and silane grafting were numbered, as shown in table 1:

| Metal | pretreatment | Sample No. |
|-------|--------------|------------|
| Copper | Polish, Remove grease with acetone | Cu (I) |
|       | Mixed solution of NaOH and (NH₄)₂S₂O₈ | Cu (II) |
|       | Mixed solution of NaOH and (NH₄)₂S₂O₈ Silane1 | Cu (III) |
|       | Mixed solution of NaOH and (NH₄)₂S₂O₈ Silane2 | Cu (IV) |

2.4. Characterization and measurement
The Total Reflection (ATR) Fourier Infrared Spectroscopy (FTIR) of the silane-modified steel surface was measured with a Spectrum BX II Fourier infrared spectrometer produced by PerkinElmer Instrument Company.

X-ray Photoelectron Spectroscopy (XPS) was measured with the PHI-5702 multifunctional electronic spectrometer, which uses the AlKa target as the radiation source, with a general energy of 29.35 ± 0.3 eV, and was calibrated with C1s285.0 eV.
The contact angle between the metal surface and water was tested with a JGW-360a contact angle tester produced by Chengde Shenghui Testing Machine Co., Ltd., and the test temperature was 25 °C. The electrochemical measurement uses a three-electrode system, a platinum mesh as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the electrolyte solution was room temperature seawater. The Electrochemical Impedance Spectroscopy (EIS) measurement was performed on a CS350 electrochemical workstation, the amplitude of the sinusoidal wave was 10mV, and its frequency range was 10mHz ~ 100kHz. The scanning step rate of the polarization curve was 2mV/s, and all potentials were relative to the saturated calomel electrode potential.

3. Results and discussion

3.1. ATR-FTIR spectrum analysis of metal surface
The curve in figure 1 represented the results of the fourier infrared spectroscopy test on the surface of the copper plate after repeated cleaning of Cu (IV) with deionized water and ethanol, as could be seen from the figure 1: There was obvious infrared absorption peaks on the surface of the plate, and relatively strong absorption peaks appear near 2974, 2872, 1712, 1667, 1541, 1109, 934, and 842 cm⁻¹, which had a similar infrared spectrum structure to the amphiphilic polymer disilane. This indicates the presence of the grafted amphiphilic polymer disilane on the surface of the metal plate.

![Figure 1. ATR-FTIR spectra of metal surfaces modified by the amphiphilic silane 2.](image)

3.2. X-ray photoelectron spectroscopy analysis of copper plates surfaces
The A and B curves in figure 2 represented the x-ray photoelectron spectroscopy on the Cu (I) and Cu (IV) surfaces, respectively. Table 2 listed the corresponding surface element composition. From table 2 and figure 2, it could be seen that Cu (IV) compared with Cu (I), the content of element C in the surface element composition was significantly increased, and the content of metallic cu element was significantly reduced, thus indicating that the amphiphilic polymer silane can be grafted onto the surface of the copper plate.

| Copper | C1s  | N1s  | O1s  | Cu2p |
|--------|------|------|------|------|
| Cu (I) | 54.56| 5.49 | 16.15| 23.80|
| Cu (IV)| 72.32| 7.62 | 7.83 | 12.23|

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Figure 2. XPS spectra of the copper surfaces without treated (A) and treated with silane 2 (B).

3.3. Measurement and analysis of copper plates surface contact angle
At 25°C, GW-360a contact angle tester was used to test the copper plates and copper plates after surface modification, shown in table 3. The contact angle of the surface of the copper plate modified by the monosilane and disilane was smaller than the contact angle of the copper plates that was not be grafted. From the relationship between the contact angle and the hydrophilicity, it could be known that the surface of the copper plates after modification, the hydrophilicity was enhanced. Because the copper plates were repeatedly washed with deionized water and ethanol before the contact angle was measured, the silane deposited on the metal surface by physical adsorption could be removed. Therefore, it was confirmed that silane could be grafted on the metal surface.

Table 3. Contact angles between copper plates surfaces and water.

| Copper | Cu (I) | Cu (II) | Cu (III) | Cu (IV) |
|--------|--------|---------|----------|---------|
| contact angle /° | 83 | 35 | 50 | 53 |

3.4. Measurement and analysis of copper electrochemical impedance spectroscopy
The Cu (I), Cu (III), and Cu (IV) were electrochemically measured. The electrochemical impedance spectroscopy (eis) was measured on a CS350 electrochemical workstation. The measurement results are shown in Figure 3.

Figure 3. Electrochemical impedance spectra of the copper surfaces modified by silanes.
These three curves were fitted using ZSimpWin software. The equivalent circuit used was R (QR). The data obtained are shown in Table 4.

**Table 4.** Fitting results of electrochemical impedance spectrum in the figure.

| Copper | Ri (Ohm.cm²) | C (μF/cm²) | n | Rct (Ohm.cm²) |
|--------|--------------|------------|---|---------------|
| Cu (I) | 23.68        | 9.980E-4   | 0.6699 | 702.8         |
| Cu (II) | 31.91       | 15.33E-4   | 0.5059 | 5222          |
| Cu (IV) | 45.57       | 2.131E-5   | 0.5100 | 6452          |

Through the analysis of figure 3 and table 4, it could be known that after the copper plates were graft-modified with amphiphilic polymer silane, the electrochemical transfer resistance on the surface of the copper plates was significantly increased, and the effect of the copper plates modified by the amphiphilic disilane was more obvious than that of the monosilane, which further confirmed that the amphiphilic polymer silane can play a certain role in inhibiting the metal plate.

**4. Conclusion**

1. The results of the XPS and ATR-FTIR, indicated that silane containing PEG segments can be uniformly grafted onto the copper surface to form a PEG brush.

2. The charge of the transfer resistance of the modified copper was increased by nearly 10 times compared with that before treatment, which indicating that amphiphilic silane had a certain corrosion inhibition effect on metal materials after being grafted onto the copper surface.

3. The decreases in contact angle of the modified copper indicated that its hydrophilic properties had been significantly improved.

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