

水基导电聚苯胺/二氧化硅杂化材料的防腐性能研究^{*}

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摘 要 利用羧基同导电聚苯胺(cPANI)主链上的氮原子的相互作用,制备了静电作用型水基导电聚苯胺/二氧化硅杂化材料,研究了杂化材料涂层对冷轧钢板的防腐性能.在 3.5% NaCl 中,含 11 wt% cPANI 的杂化材料涂层的腐蚀电位比纯二氧化硅涂层正移了 200 mV,腐蚀电流从 13.4 μ A 降到 2.4 μ A,下降了 5 倍,表明含 cPANI 的静电作用型杂化涂料使冷轧钢板表面变得更惰性.阻抗分析结果表明,cPANI 含量为 11 wt% 的静电作用型杂化材料的阻抗比纯无机二氧化硅涂层大一个数量级,而且在碱性介质中浸泡 10 天后,杂化材料涂层的阻抗仍然保持稳定,而纯无机二氧化硅涂层的阻抗比初始值下降了一个数量级.杂化材料的形态分析结果表明,cPANI 在静电作用型 cPANI/二氧化硅杂化材料中的分布比普通 cPANI/二氧化硅杂化材料中更加均匀一致,从而使得它比普通的 cPANI/二氧化硅杂化材料具有更好的防腐效果.

关键词 水基导电聚苯胺,杂化材料,腐蚀防护,水性涂料

WATER BORNE ANTI-CORROSION COATING FROM CONDUCTIVE POLYANILINE/POLYSILSESQUOXANE HYBRIDS^{*}

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Abstract Water borne anti-corrosion coating was prepared from conductive polyaniline (cPANI)/polysilsesquioxane hybrids, where electrostatic interaction was introduced into the hybrids by carboxyl group capable of interacting with positively charged nitrogen atom in cPANI backbone. In 3.5 wt% NaCl media, the corrosion potential of the electrostatic-interaction hybrid coating containing 11 wt% cPANI showed nearly 200 mV positive than that of pure inorganic polysilsesquioxane coated cold rolled steel (CRS), with corrosion current dropping by 5 times from 13.4 μ A to 2.4 μ A, indicating that the cPANI hybrids coated CRS became more noble against the electrochemical corrosion. The Niquist plots indicated that electrostatic-interaction hybrid coating with 11 wt% cPANI displayed impedance one order of magnitude higher than that of pure inorganic coating, moreover, the impedance of the cPANI/polysilsesquioxane film maintained nearly constant after 10 days of immersion in saline media, whereas that of pure inorganic coating decreased one order of magnitude from the initial value, suggesting much improved anti-corrosion performance using the electrostatic-interaction cPANI hybrids. Morphology study indicated that the cPANI was distributed in a more homogeneous way in electrostatic-interaction cPANI/polysilsesquioxane hybrids than in common cPANI/polysilsesquioxane hybrids, leading to much better anti-corrosion performance than common cPANI/polysilsesquioxane hybrids.

Keywords Conductive polyaniline, Sol-gel hybrids, Corrosion protection, Water borne coating

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1 INTRODUCTION

Polyanilines have been widely studied for their unique electrical, electrochemical and thermal properties^[1,2]. Coatings containing polyaniline have been made from organic solutions or dispersions^[3-6], or even from solvent free system^[7], passive films are found on the interlayer between metal and organic coating in corrosive media, and the anti-corrosion behavior of polyaniline has been confirmed^[8]. Now polyaniline anti-corrosion coatings are regarded as possible candidates to replace environmentally unfavorable chromium-containing or zinc-rich coatings^[9-13]. Owing to restrictions on organic solvents from environmental concern, anti-corrosion coatings from water borne polyaniline solution or dispersion are very attractive. In this group, polyaniline has been made water soluble employing a phosphate dopant bearing a long hydrophilic tail^[14]. Since phosphates are known as corrosion inhibitor for steel^[11,15], this water borne conductive polyaniline may be more effective in corrosion protection. However, such water borne polyaniline coatings generally have poor water resistance in that it may break into pieces upon water soaking. Recent development on this water borne cPANI was the preparation of cPANI/polysilsesquioxane hybrids by a sol-gel process to improve its water resistance, thermal stability and mechanical properties^[16-21], but none of them concern the anti-corrosion property of the hybrids. Polysilsesquioxanes, generally characterized by the empirical formulas ($\text{RSiO}_{3/2}$), where R is an organic group which is linked with silicon atom by unhydrolyzed carbon-silicon bond, have been regarded as interesting nanoscale building units for organic-inorganic hybrid materials. In addition, the organic group can react with many organic chemicals to fabricate covalent or non-covalent organic-inorganic hybrids^[22,23]. Polysilsesquioxane coatings exhibit increased flexibility and thickness compared with their inorganic counterparts and have been found to provide good corrosion resistance for metal substrates because of their barrier properties^[24,25]. Therefore, in this report, a cPANI/polysilsesquioxane hybrid coating was prepared, where electrostatic interaction was

introduced into the hybrids by carboxyl group capable of interacting with positively charged nitrogen atom in cPANI backbone, and its anti-corrosion performance on CRS in saline media was evaluated.

2 EXPERIMENTAL

2.1 Materials

Maleic anhydride (MAH), aminopropyltriethoxysilane (APTES) and methyltriethoxysilane (MTES) were of analytical purity from Acros Co., polyaniline in emeraldine base (PANI) was the product of Hunan Ben'an Co. licensed under this laboratory.

2.2 Preparation of Conductive Hybrids

The water soluble cPANI was prepared according to earlier work in this group^[14]. The hydrolysis-condensation of MTES was carried out employing aminolysis product of MAH and APTES (the ratio of MTES/MAH/APTES was kept 4 : 1 : 1) as catalyst, and the molar ratio of $-\text{Si}(\text{OR})_3$ /ethanol/water was 1/5/4. The solution was then added dropwise stoichiometrically to the aqueous conductive polyaniline solution at 50°C under vigorous stirring. The mixture was stirred for another 4 h before film casting at room temperature. After gelation, the samples were transferred to oven at 50°C for curing. The thickness of final films was around 40 μm . The common cPANI/polysilsesquioxane hybrids for reference were prepared employing MTES as precursor without MAH-APTES.

2.3 Measurements

All electrochemical measurements were performed at room temperature on a Solartron 1287 electrochemical interface analyzer with platinum wire as counter electrode and Ag/AgCl/1 mmol/L KCl as reference electrode. The CRS coupons coated with various samples were used as working electrodes, and their working surface area was set as 1 cm^2 using a Teflon holder to avoid the edge effect. The electrolyte solution was 3.5 wt% NaCl solution. Polarization resistance (R_p) was measured by sweeping the applied potential from 20 mV below to 20 mV above the corrosion potential (E_{corr}) at a scan rate of 1 mV/s to record current change. The R_p value was obtained from the slope of the potential-current curve. The Tafel plots were generated by scanning the potential from 250 mV

below to 250 mV above the E_{corr} at a scan rate of 1 mV/s. The corrosion current (I_{corr}) was determined by superimposing a straight line along the linear part of the cathodic or anodic curve and extrapolating it through E_{corr} . Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 kHz ~ 0.01 Hz. The working electrode was first maintained in test environment for 30 min to reach an equilibrium state before the impedance run. The morphologies of the conductive films were examined by a JEOL-JXA-840 scanning electron microscope (SEM). The adhesion strength of the hybrids on CRS substrate was measured on QFH graft scratch instrument according to China National Standard GB/T 9286-1998. The rating was classified as 6 grade, "grade 0" indicated a smooth and intact cut edge on the cross cut of the tested coating film, where no part of cross cut film was stripped by a neutral stripper (width of 25 mm with adhesive force of (10 ± 1) N/25 mm), "grade 1" indicated that the failure area was below 5% of the whole area, and the failure area was over 5% but below 15% of the whole area for "grade 2", "grade 3" described that the failure area was over 15% but below 35% of the whole area, the failure area was over 35% but below 65% of the whole area for "grade 4", for "grade 5", the failure area was more severe than that described in "grade 4". Generally, "grade 0" to "grade

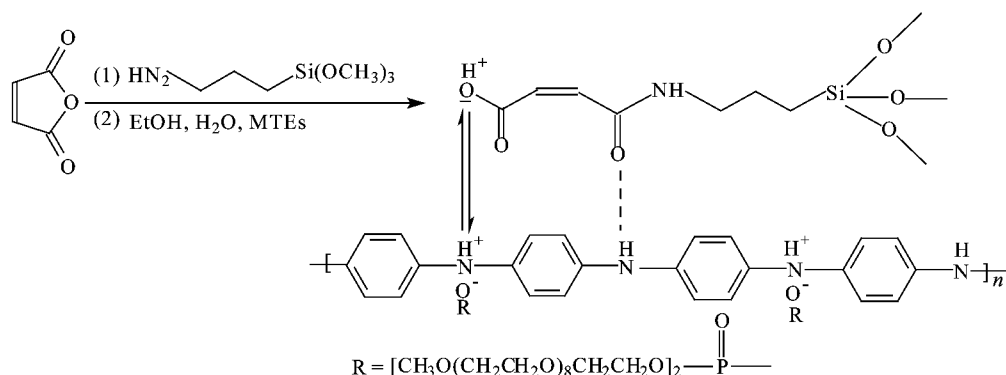
3" may be qualified for painting and varnishes.

3 RESULTS AND DISCUSSION

3.1 Formation of Electrostatic Interaction Hybrids

As shown in Scheme 1, after the aminolysis of MAH and APTES and hydrolysis of the $-\text{Si}(\text{OR})_3$ of APTES and MTES, the polysilsesquioxane precursor bearing the carboxyl group was generated, and then mixed with an aqueous solution of cPANI to afford a homogeneous solution for film casting. Upon gelation (crosslinking) and drying, the polysilsesquioxane network was obtained, and the polyaniline chains were entrapped in the inorganic network. The electrostatic interaction was thus introduced into the hybrids by carboxyl group linked to polysilsesquioxane network which is capable of interacting with positively charged nitrogen atom in cPANI backbone.

The characterization of the electrostatic-interaction cPANI hybrids, such as electrical conductivity, UV-Vis, FTIR spectra and ^{29}Si -MAS NMR has been reported in our previous work^[20]. By analyzing its spectrum, NMR data, morphology and electrical conductivity, the electrostatic interaction was confirmed to exist between cPANI and polyaniline in this cPANI hybrids^[20].



Scheme 1 Electrostatic interaction in cPANI/polysilsesquioxane hybrids

3.2 Corrosion Protection Properties

The Tafel plots for various samples are shown in Fig. 1, and the corresponding electrochemical parameters are summarized in Table 1. Pure cPANI film showed little corrosion protection to CRS coupon. It

is reasonable considering its poor water resistance which makes it easy for the corrosive elements to penetrate cPANI film and reach CRS substrate. As shown in Table 1, compared to the bare CRS coupon, the CRS coated with pure inorganic coating showed a

higher E_{corr} value and a lower I_{corr} value which should be due to the physical barrier characteristics of the coating, however, it exhibited a lower E_{corr} value and a higher I_{corr} value than the CRS coated with cPANI/polysilsesquioxane hybrid coatings. For example, with 8 wt% of cPANI loading, the electrostatic-interaction hybrids coated CRS has a much higher E_{corr} of -0.365 V and a much lower I_{corr} of $3.7 \mu\text{A}$, respectively. Moreover, corrosion potential increased to -0.352 V, when cPANI loading increased to 11 wt%, nearly 300 mV positive than that of uncoated CRS, indicating that the cPANI hybrids coated CRS became more noble against the electrochemical corrosion compared with pure inorganic coating. Correspondingly, the polarization resistance (R_p) was $5.35 \times 10^3 \text{ k}\Omega \cdot \text{cm}^2$ when cPANI loading was 11 wt%, which was one order of magnitude higher than that of pure inorganic polysilsesquioxane coated CRS, indicating much improvement in anti-corrosion behavior. However, when cPANI loading increased to 18 wt%, E_{corr} and I_{corr} became -0.409 V

and $5.2 \mu\text{A}$, respectively. The weakened corrosion protection performance was consistent with the deteriorating water resistance of the hybrid coating, since excessive cPANI disturbed the three dimensional network of the hybrids and thus reduce the water resistance of the hybrid film^[20].

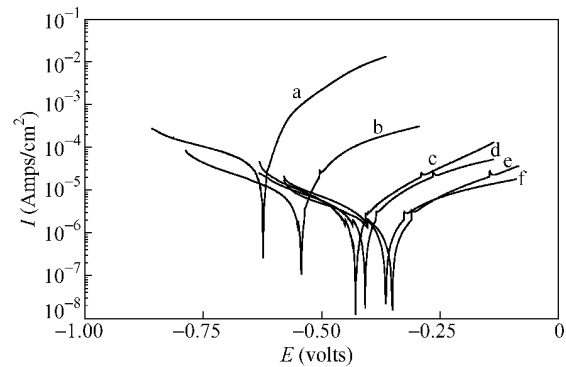


Fig. 1 Tafel plots of (a) pure cPANI coating, (b) pure inorganic coating, (c) common cPANI/polysilsesquioxane hybrid coating containing 11 wt% cPANI, and (d ~ f) electrostatic-interaction cPANI/polysilsesquioxane hybrid coatings with cPANI weight loadings of 18%, 8%, and 11%, respectively

Table 1 Electrochemical parameters of various samples in 3.5 wt% NaCl solution

Sample	Composition (wt%)		Electrochemical parameter		
	cPANI	PANI	E_{corr} (V)	I_{corr} (μA)	R_p ($\text{k}\Omega \cdot \text{cm}^2$)
Bare	—	—	-0.641	39	4.2
Pure cPANI	100	13.5	-0.624	26.7	8
Pure inorganic coating	0	0	-0.544	13.4	215
Electrostatic-interaction cPANI hybrids	18	2.4	-0.409	5.2	2.26×10^3
	11	1.5	-0.352	2.4	5.35×10^3
	8	1.1	-0.365	3.7	3.18×10^3
Common cPANI hybrids	11	1.5	-0.428	4.1	1.52×10^3

Figure 2 shows the Nyquist diagram of various samples, a semicircle characteristic of transport resistance through the coating was observed for each sample. The impedance of pure cPANI coating was too small to be observed in the Nyquist diagram, consistent with its poor corrosion protection property. The electrostatic-interaction hybrid coating with 11 wt% cPANI displayed the highest impedance, one order of magnitude higher than that of pure inorganic coating, suggesting improved anti-corrosion performance, which was consistent with the result from above Tafel plots.

Figures 3 and 4 show the Bode curves of the electrostatic-interaction cPANI hybrid coating and pure inorganic coating in saline solution, respectively. After

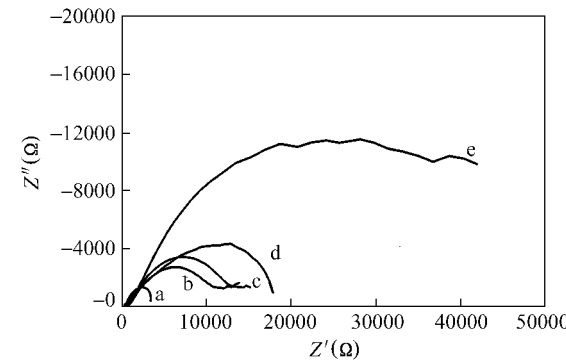


Fig. 2 Nyquist plots of (a) pure inorganic coating, (b) common cPANI/polysilsesquioxane hybrid coating containing 11 wt% cPANI, and (c ~ e) electrostatic-interaction cPANI/polysilsesquioxane hybrid coatings with cPANI weight loadings of 18%, 8%, and 11%, respectively

10 days of immersion in saline media, as shown in Fig. 3, the impedance of electrostatic-interaction cPANI/polysilsesquioxane film maintained nearly constant, demonstrating good protection ability, whereas

for pure inorganic coating, as can be seen in Fig. 4, the impedance decreased one order of magnitude from the initial value of $2.4 \times 10^3 \Omega \cdot \text{cm}^2$ to $2.1 \times 10^2 \Omega \cdot \text{cm}^2$.

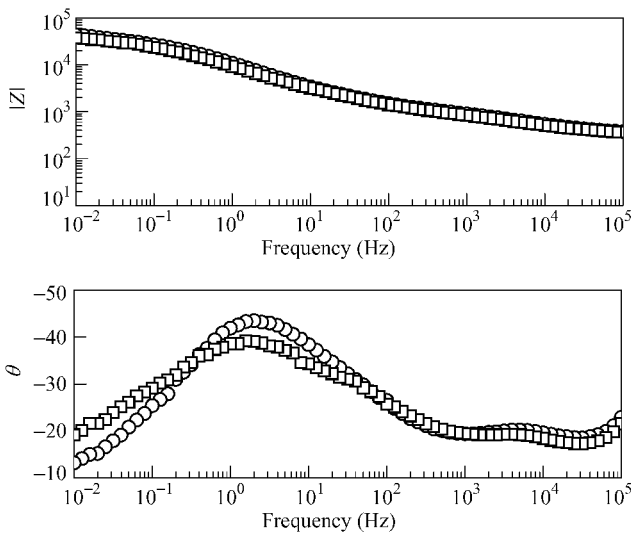


Fig. 3 Bode curves of electrostatic-interaction cPANI/polysilsesquioxane hybrid coating with 11 wt% cPANI in 3.5 wt% NaCl solution for 1 h (circle-open) and 240 h (square-open)

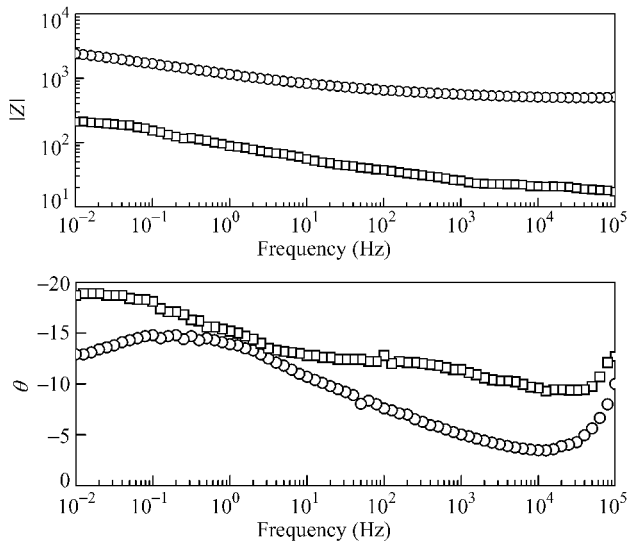


Fig. 4 Bode curves of pure inorganic coating in 3.5 wt% NaCl solution for 1 h (circle-open) and 240 h (square-open)

3.3 Possible Reasons for Improved Corrosion Protection Performance

According to the literatures and our earlier publications, the redox property of cPANI was very important in corrosion protection^[1-6,13]. Since the redox potential of polyaniline was much higher than that of iron, iron was first oxidized to Fe^{2+} or Fe^{3+} and further to iron oxides, polyaniline emeraldine salt (PANI-ES)

was reduced to polyaniline leucoemeraldine salt (PANI-LS) with the concomitant release of phosphate dopant, PANI-LS then underwent re-oxidation by dissolved oxygen in media to PANI-ES. Due to the quasi-reversible reaction, a passive metal oxide layer on the surface of metal was formed to protect CRS from being corroded, offering enhanced corrosion protection efficiency. As far as pure inorganic coating was

concerned, no redox active component existed, physical barrier effect was the only factor, so the protection property of the coating decreased once this barrier effect was overcome, which was clearly observed in Fig. 4 where the impedance of the coating decreased after immersion in saline media for 10 days.

The better adhesion on CRS substrate was also important to improve the anti-corrosion behavior of the coating. The adhesion of the coating on CRS substrate was measured and shown in Table 2. The electrostatic-interaction cPANI hybrid coating and common cPANI hybrid coating showed grade 1 and 2 in adhesion, respectively, whereas that of pure inorganic coating was in grade 3. It should be noted that phosphate group could act as adhesion promoter for metal, fortunately cPANI consisted of polyaniline in 13.5 wt% and phosphate in 86.5 wt%, therefore, the phosphate in the hybrids could enhance the adhesion strength between the hybrid coating and CRS.

Table 2 Adhesion strength of the cPANI/polysilsesquioxane hybrid coating and pure inorganic coating on CRS substrate

Coating	cPANI (wt%)	Phosphate dopant (wt%)	Adhesion (grade)
Electrostatic-interaction cPANI hybrids	18	15.5	1
Common cPANI hybrids	18	15.5	2
Pure inorganic coating	0	0	3

As can be seen from Fig. 1, Fig. 2 and Table 1, even the PANI loading was similar, the electrostatic-interaction cPANI/polysilsesquioxane hybrid coating demonstrated better anti-corrosion performance than the common cPANI hybrid coating without electrostatic interaction. The introduction of electrostatic interaction could change the interaction level between the two components, which led to different dispersing degree of cPANI in the matrix. The strong electrostatic interaction between cPANI and inorganic phase helped the cPANI chain to be distributed and confined evenly into the inorganic matrix, leading to conductivity percolation threshold as low as 8 wt% of cPANI loading^[20]. When cPANI loading was above 8 wt%, conducting network can be formed to passivate metal surface against further corrosion, therefore it was reasonable for the good anti-

corrosion behavior of the hybrid film even in quite low cPANI loading. Whereas for the common cPANI hybrid film without electrostatic interaction, the poor interaction and lower compatibility between cPANI and inorganic phase led to phase separation between the two components, and apparent aggregation of cPANI can be observed, resulting in a coarse surface in contrast to the smooth and dense surface of the electrostatic-interaction hybrid film.

To our expectations, SEM of the electrostatic-interaction cPANI/polysilsesquioxane hybrid film (Fig. 5a) revealed a compact fibrillated morphology, while a coarse granular structure was observed for the common cPANI hybrid film (Fig. 5b), indicating that electrostatic interaction really helped cPANI to be well dispersed in inorganic matrix. Besides, as discussed above, the phosphate dopant of cPANI can serve as adhesion promoter, thus the better dispersion of phosphate dopant in the electrostatic-interaction hybrid coating could lead to higher adhesion strength than the common cPANI hybrid coating, which was confirmed by the result of scratch test as shown in Table 2.

Therefore, cPANI was distributed in a more homogeneous way in the electrostatic-interaction cPANI/polysilsesquioxane hybrid coating, leading to much better anti-corrosion performance than the common cPANI hybrid coating.

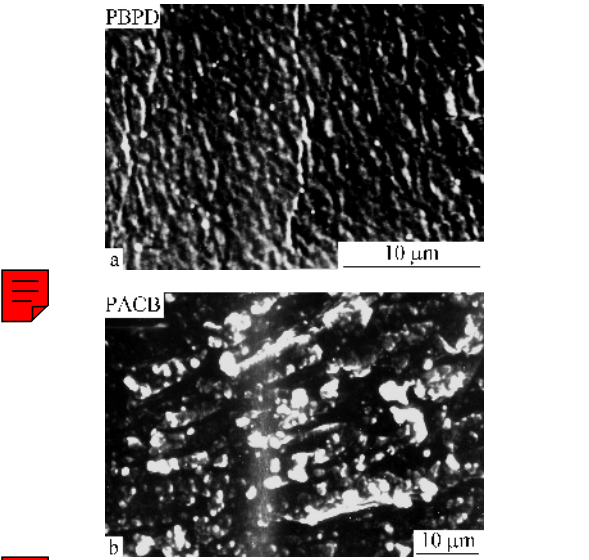


Fig. 5 SEM images of cPANI hybrids with electrostatic interaction (a) and without electrostatic interaction (b) cPANI loading in all samples was 20 wt%

Although compared with other cPANI composite coating cast from organic solvent^[10~13], the anti-corrosion efficiency of this electrostatic-interaction cPANI/polysilsesquioxane hybrid coating is not so high, which may be attributed to unoptimized preparation conditions,the usage of water as solvent in this cPANI hybrid system makes it very attractive.

4 CONCLUSIONS

The electrostatic-interaction cPANI/polysilsesquioxane

hybrid coating prepared from aqueous media showed remarkable enhancement in corrosion protection of CRS in saline media,even cPANI content in the coating was just above 8 wt% . Three possible factors, redox behavior of PANI, improved adhesion strength and uniform dispersion of cPANI in inorganic matrix, were discussed for the improved anti-corrosion performance.

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