Improved corrosion performance of electrophoretic coatings by silane addition

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ABSTRACT

Organosilanes are incorporated into a commercial cathodic electrophoretic paint, resulting in significant improvement in the long-term corrosion protective properties of the paint. The addition of organosilanes have strengthened mechanical properties, improved hydrophobicity, lowered water uptake and less decrease in glass transition temperature of the coatings, suggesting the enhancement in bulk structure of the polymeric coatings. In addition, silane-enriched layer preferentially forms at the metal/coating interface during the electrophoresis process, leading to better adhesion between the substrate and the coating. The structural enhancement in both the coating and the metal/coating interface explains the improved corrosion performance of silane-incorporated electrophoretic coatings.

1. Introduction

Organic coatings are most commonly and widely used approaches in protecting metallic substrates against deterioration. Basically, organic coatings comprise at least two individual layers, each of them provides unique functionality. On the one hand, the primer layer offers barrier functionality and provides corrosion inhibition effect owing to the pigments contained in the layer; on the other hand, the underlying pre-treated thin conversion layer provides enhanced adhesion between the substrate and the primer. The conventional processes mainly use hexavalent chromium compounds in the conversion layer and chromium or other heavy metal ions as the active corrosion inhibitors in the primer. Despite of the excellent corrosion protection properties offered by this traditional paint system, the use of hexavalent chromium compounds, which are known to be highly carcinogenic and strongly toxic, is restricted by more and more countries [1–6].

Silanization based on the use of alkoxysilanes has emerged as an environmental compliant alternative for chrome conversion layer in metal pretreatment industry [2,7–10]. The formation of silane films is a result of the sol–gel processes [11], i.e. the hydrolytic reaction of silane reagents producing silanol (SiOH) (reaction (1)) and the condensing reactions among silanols themselves (reaction (2a)) and between silanols and hydrolated metallic substrates (reaction (2b)) forming Si–O–Si and Si–O–Metal covalent bonds.

\[
R - Si - O'R' + H_2O \rightarrow R - Si - O - Si - R + H_2O \quad (2a)
\]

\[
R - Si - OH + M - OH \rightarrow R - Si - O - M + H_2O \quad (2b)
\]

where R and R' are functional groups and alkyl groups, respectively, and M represents the metal substrates. The former reaction (reaction (2a)) not only determines the barrier performance of the films and thereby their short-term protective function, but also predicts the potential of coupling reactions between silane and the up-coated primer. The latter reaction (reaction (2b)) provides strong adhesion to the substrate due to the formation of covalent bonds [12]. Although the large scale industrial use of silanization still remains uncertain, extensive work has been done on silane films alone or on silane films/organic coating anti-corrosion system in the last decade [1,12–17].

Unlike the above-mentioned two-step process in constructing silane films/organic coating system, one-step use of silane agents in paint system might be more attractive. van Ooij group developed a one-step “superprimer” system [18,19], formulated using a mixture of acrylate and epoxy resins, organofunctional silanes, and a cross-linker, using for corrosion protection of aluminum and galvanized steel. This novel system demonstrated excellent potential as replacement for the currently used chrome-based technology. The protection mechanism of the “superprimer” was then studied by Wang and Schafer using neutron reflectivity technology [20]. showing that silane component enhanced both the substrate/coating interface structure and the chemical structure of primer. Furthermore, our previous work showed that the corrosion performance of the one-step silane-incorporated epoxy coating could be further improved by chemically grafting silane...
molecules onto epoxy backbone structure with the aid of an organic tin catalyst [21–24].

One has already noticed an advance in deposition technique of silane films invented by Mandler group [25], i.e. the electrochemically assisted method. The mechanism of cathodic electrodeposition is based on the catalyzed condensation reactions (reactions (2a) and (2b)) by the cathodically generated OH ions near the electrode surface [25]. This technique has found its application in preparing better anti-corrosive organosilane films [26–33], because, compared to conventional dip-coating method, electrodeposition leads to denser and thicker silane films under appropriate deposition conditions, especially the deposition potential [28–30].

As an advancement of the one-step silane-based superprimer, we present in this study the electrochemical formation of a "superprimer". To meet the requirement of electrochemical electrocoating technique, the coating system was formulated based on commercially available cathodic electrophoretic epoxy resin and two different organosilanes including bis-1,2-triethoxysilylhexene (BTSE) and methyltrimethoxysilane (MTMS). The electrophoretic coating has numerous advantages over other coating system [34,35], particularly its high materials utilization (>95%), low level of pollution (water-borne) and ease of automation, thus it has been extensively used in the automotive industry. As will be presented in this study, this new "superprimer" system exhibits excellent anti-corrosion performance in protecting galvanized steels. The potential role of silane component in the electrosytoped superprimer is discussed.

2. Experimental

2.1. Materials and chemicals

Galvanized steel sheets (kindly supplied by Baosteel Co. Ltd., Shanghai, China) with zinc deposit of ~5 μm were used as the substrates. The sheets were degreased in home-made surfactant-based alkaline solution for 15 min at 60 °C, another 15 min of sonication in acetone and then washed with de-ionized (DI) water, and finally blow-dry with warm air. Two kinds of silanes were used in this study, one is BTSE (purity > 95.0%, Wuha Chemical, Wuhan, China) and the other is MTMS (purity > 97.0%, Zhejiang Research Institute of Chemical Industry Ltd., Hangzhou, China). Both were used as received without further purification. The cathodic electrophoretic paint (HL-15001B, purchased from Haolisen Paint Co. Ltd., Shanghai, China) consists of a lead-free cathophoretic epoxy resin (solid content: 45.0 ± 3.0 wt%); solvent content: 1.2–2.5 wt%; water: bal.; electrolytic conductivity at 25 °C at 10 wt% solid content: 1200 μs cm⁻¹. Prior to electrophoresis, the commercial electrophoretic paint was pre-diluted with DI water to get a precursor containing 10 wt% solid content. Silane reagent with different weight percentages, with respect to the total weight of precursor, was mixed into the precursor under aggressive stirring condition for 30 min to prepare silane-involved electrophoretic paint precursors.

2.2. One-step electrodeposition of silane-incorporated electrophoretic paint

Prior to the preparation of coating, galvanized steel was sealed with adhesive tape to leave a 40 mm × 30 mm exposed area on one side as the working electrode, and a large graphite sheet was used as the counter electrode. Both the electrodes, separated from each other with a distance of 10 cm, were immersed into precursors. A voltage of −60 V was applied between the galvanized steel and the graphite sheet at 25 °C for 3 min. After that, the coated galvanized steel was rinsed with DI water and pre-dried in atmosphere at 50 °C for 5 min then cured at 180 °C for 15 min. The thicknesses of the coatings obtained were 43 ± 5 μm, as measured by induced eddy current technique. All painted samples were kept in a desiccator for at least 1 week before the tests.

2.3. Electrochemical impedance spectroscopy (EIS) measurements

EIS was used to evaluate the corrosion electrochemical properties and water uptake behavior of the coated samples. The measurements were performed on a M273 potentiostat (Princeton Applied Research, USA) combined with an MS210 lock-in amplifier (Signal Recovery, USA). Three-electrode system was used, with the coated sample as the working electrode (exposure surface area of 10 cm²), a Ag/AgCl (in saturated KCl) electrode as the reference and a platinum plate as the counter electrode. The impedance measurements were carried out over a frequency range from 100 kHz to 10 mHz with an AC excitation amplitude of 10 mV at the open circuit potential. For testing of water uptake, the frequency range was selected from 100 kHz to 1 Hz. All the measurements were conducted at 25 °C in 3.5 wt% NaCl aqueous solution. The experimental data were analyzed using the commercial software Zview.

2.4. Accelerated test

Salt spray test, SST, was carried out to evaluate the corrosion performance and wet adhesion properties of the electrophoretic coating, with the guidance of ASTM 1654-92. A defect was introduced into the coated samples using a scribing tool with a metal tip prior to SST. The defect was about 4 cm in length and penetrated all the way through to the bare metal. 50 g of NaCl solution (pH 7.0) was atomized in a salt spray cabinet at 35 °C. The tested samples were placed at an angle of 45° in the cabinet, exposed to the fog for a certain period.

Boiling water test was also employed to evaluate the adhesion properties of coatings. The coated samples were immersed in boiling water for 6 h. After completion of the test, the corrosion protection property of the coatings was quantitatively measured by EIS under the same conditions as described in Section 2.3.

2.5. Physicochemical characterizations

The hardness and Young's Modulus of the electrophoretic coatings samples were measured by DUH-211S dynamic ultra hardness tester (Shimadzu, Japan) according to ISO 14577-2007. The corresponding values were calculated by averaging the measured data at three randomly selected spots. The contact angle of the fresh coatings were measured in the air by JC2000X A static droplet contact angle measuring instrument (Shanghai, China) with high speed CCD camera for image capture. DI water drops with the volume of about 15 μL were used. Contact angles were calculated as the average of measured data at five randomly selected spots. Differential scanning calorimetry (DSC) was employed to determine the glass transition temperature (Tg) of the electrophoretic coatings before and after immersion in NaCl aqueous solution. The measurements were carried out on a Delta Series DSC7 Thermal Analysis System (Perkin-Elmer Corp., USA) in a nitrogen atmosphere with a scanning rate of 20 °C min⁻¹ in the temperature range from −30 to 100 °C. The whole measurement process was carried out according to ASTM D3418-82. Fourier transform reflectance-absorption IR (ATR-FTIR) was used to characterize the interface and bulk chemical structure of the electrophoretic coating. Infrared spectra were recorded on a Nicolet 470 spectrophotometer (Thermo Nicolet, USA). Signals of 64 scans at a resolution of 8 cm⁻¹ were averaged before Fourier transformation.
3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

EIS is a rapid, non-destructive and convenient technique for the evaluation of corrosion behaviors of organic coated metals [36–40]. Fig. 1 shows the EIS spectra obtained for BTSE-incorporated electrophoretic coatings after exposure to 3.5 wt.% NaCl for 9 days. The data of the sample painted with pure electrophoretic coating are also shown in the figure as the control. The impedance spectroscopy of the control presents 3 time constants in high, intermediate and low-frequency domains, respectively (curve 1 in Fig. 1b), indicating the existence of corrosion reactions under the organic coatings. The incorporation of only a small amount of BTSE, e.g., 0.1 wt.%, leads to the elimination of low-frequency relaxation (curve 2, Fig. 1b). When the BTSE concentration increases to 0.3 wt.%, both the intermediate- and the low-frequency relaxations disappear (curve 3, Fig. 1b), suggesting the absence of active corrosion reaction beneath such a modified coating due to its high barrier performance. The BTSE-incorporated coating system shows an obvious increase in phase angle (Fig. 1b) and, more importantly, significant increase in impedance value across the frequency domain (Fig. 1a). The above-described phenomenon definitely shows that the incorporation of BTSE into the electrophoretic coatings can dramatically improve their corrosion performance. However, the incorporation with an excessive amount of BTSE, e.g., 1.0 wt.% BTSE, gives a negative effect (curve 4, Fig. 1).

Similar phenomena can be found if one chooses MTMS as the additive of electrophoretic coatings (impedance data not shown). Fig. 2 summarizes the effect of incorporating these two silane reagents on the corrosion performance of the modified coatings which is quantitatively evaluated by the low-frequency impedance module (\(|Z|_{f = 10 \text{ mHz}}\)). The figure clearly shows that the incorporation of either BTSE or MTMS dramatically enhances the corrosion properties of the electrophoretic coatings, while BTSE is much more effective than MTMS. This can be seen from the much higher impedance values of BTSE-modified coating system (curve 1). To describe more quantitatively, the highest value of \(|Z|_{f = 10 \text{ mHz}}\) at 0.3 wt.% of BTSE incorporation is 2 orders of magnitude higher than that of the coating sample without BTSE addition, however the optimal incorporation of MTMS of 0.5 wt.% can only give 1 order of magnitude higher in \(|Z|_{f = 10 \text{ mHz}}\) (curve 2).

The information about intrinsic coating properties and electrochemical behaviors at the coating/metal interface can be obtained by numerical fitting of the EIS data to an appropriate equivalent electrical circuit (EEC). Many EECs have been proposed in literatures for organic coated metal systems [36,37,41]. Here, we employed three classical EECs for the fitting of EIS spectra obtained at different immersion stages (Fig. 3). Model (a) is used when the coated sample is at its initial immersion, and during this stage, the electrolyte has not arrived at the metal substrate. Under this circumstances, the coating demonstrates excellent barrier behaviors and the impedance spectra reveal only one capacitive loop with a large radius. The circuit is composed of coating capacitance \(C_c\) parallel to the electrolyte resistance in the pores of the coating \(R_{po}\). Model (b) is selected when the electrochemical reaction occurs due to the arrival of the electrolyte. The new \((R_{po}C_c)\) relaxation is attributed to the charge-transfer resistance and double-layer capacitance, respectively. Model (c) is suitable for the case of intensive corrosion reaction, resulting in the formation of pronounced amount of corrosion products. The mass transport of these products may be restricted through the micro-pores channels of the
coating to the bulk solution. \((R_{\text{imp}} C_{\text{cap}})\) combination defined as the diffusion resistance and the diffusion capacitance, respectively, is proposed to complete this circuit. To obtain more precise fitting results, capacitive elements \((C)\) in the EECs are all replaced by constant phase elements (CPE). The impedance of a CPE can be described as:

\[
Z_{\text{CPE}} = \left( Y_0(\omega) \right)^{-1}.
\]

where \(Y_0\) is CPE constant, \(n\) is the CPE coefficient with the value between \(-1\) and \(1\) (being \(1\) for an ideal capacitor) and \(\omega\) is angular frequency.

As the examples, Fig. 1 also gives fitting results of these typical impedance data by using appropriate EECs. The electrode covered with pure electrophoretic coating is fitted to model (c) and the samples of 0.1 and 0.3 wt.% BTSE-incorporated coatings are fitted to models (b) and (a), respectively. All the experimental data can be fitted well. It should be noted that the EEC used may be varying during the immersion. The comparison of the fitting determines which model is selected [42].

Fig. 4 displays the changes of four typical electrical parameters \((C, R, C_{\text{cap}}\) and \(R_{\text{imp}}\)) with the immersion time. \(C\) and \(R\) measure the barrier properties of organic coatings against the penetration of water and ions, \(C_{\text{cap}}\) is an indicator of water uptake in the coating. It increases during the water uptake due to much higher dielectric constant of water (\(\sim 80\)) with respect to that of polymeric materials (\(\sim 2-8\)) [43,44]. More detailed demonstration will be given below. \(R_{\text{imp}}\) is a measure of the total resistance of electrolyte in the micropores. Fig. 4a and b clearly shows that the incorporation of BTSE improves the resistances against both the water uptake and ions penetration.

\(C_{\text{cap}}\) and \(R_{\text{imp}}\) are the parameters directly related to the corrosion performance of the coated samples, because they are a measurement of the total number of active sites for electrochemical corrosion reaction at metal/electrolyte interface. \(C_{\text{cap}}\) increases and \(R_{\text{imp}}\) decreases after the immersion due to the expansion of the active site (Fig. 4c and d). The incorporation of BTSE slows down the deterioration process of electrochemical interface. Furthermore, the comparison between Fig. 4b and d shows that after BTSE incorporation, \(R_{\text{imp}}\) increases to a much higher extent than \(R_{\text{imp}}\), does, probably suggesting that the inhibition role of silane component is dominant at metal/electrolyte interface with respect to the bulk coatings. MTMS incorporation shows similar results, that is, both improve the barrier performance of bulk electrophoretic coatings and dominantly inhibits the corrosion reaction at the metal/coating interface (data are not shown here).

The quantitative calculation of water uptake is done according to Brasher-Kingsbury's equation (Eq. (4)) assuming the transport process of water is controlled under Fickian diffusion [45]. In Eq. (4), \(\phi_w\) is the volume fraction of water in organic polymers, \(C_i\) is the coating capacitance at immersion time \(t\), \(C_{\text{cap}}\) is the dry coating capacitance and \(e_\infty\) is the dielectric constant of water.

\[
\phi_w = \frac{\log(C_i/C_{\text{cap}})}{\log e_\infty}\quad (4)
\]

Coating capacitance is obtained by numeric fitting of EIS data. In order to get more experimental data, fast EIS measurement is carried out for water uptake detection by choosing the frequency range from \(100\) kHz to \(1\) Hz. The result is shown in Fig. 5a. It shows that in the early stages of immersion \((0-20\) h), the water uptake values increase steeply and linearly with the square root of time \((t^{1/2})\) for both the pure and silane-incorporated coatings, denoting a fast Fickian diffusion of water into the coatings [41]. And then, a saturation plateau is observed after ca. 24 h of immersion, indicating the water uptake reaches a quasi steady value. After that, \(\phi_w\) dramatically increases again for the pure coatings, probably due to the change of diffusion kinetics [42]. However, for the silane-incorporated coatings, \(\phi_w\) only shows very slight increase after the plateau. The figure shows that only low concentrations of silane can remarkably reduce the adsorption of water in the electrophoretic coatings. Water diffusion coefficient \((D)\) in the coating can be obtained from the time dependence of coating capacitance in the case of Fickian diffusion during the initial immersion stage by using the following equation:

\[
\ln C_i - \ln C_{\text{sat}} = \frac{2\sqrt{D \pi}}{\pi \sqrt{t}}
\]

where \(C_i\) is the coating capacitance at time \(t\), \(C_{\text{sat}}\) the coating capacitance at saturation, and \(t\) the coating thickness. Fig. 5b summarizes the calculated results of \(D\) in BTSE and MTMS-incorporated coatings. For both two silanes-involved coatings, \(D\) decreases first and then increases when the silane content increases. The lowest \(D\) is obtained at 0.3 wt.% BTSE and 0.5 wt.% MTMS, respectively, which is in good agreement with the optimal content values in the low-frequency impedance measurement (Fig. 2). Fig. 5b also shows that the incorporation of BTSE always gives lower water diffusion coefficients with respect to that of MTMS, indicating better barrier performance of the BTSE-involved coatings. The values of \(D\) calculated are found to be \(1.7-5.4 \times 10^{-10}\) cm²/s, which are in the range of \(10^{-10}-10^{-12}\) cm²/s for organic coatings with good barrier performance at room temperature reported in literature [46].

3.2. Accelerated corrosion test

SST is used to directly evaluate the corrosion performance of the silane-incorporated electrophoretic coatings. For the pure electrophoretic coating, pronounced amount of white zinc corrosion products and many blisters are visible along two sides of the defect after 850 h SST, which indicates serious corrosion reactions occur on the scribe. However, much fewer blisters and corrosion products can be seen on the samples covered with silane-incorporated coatings. Especially for the sample covered with 0.3 wt.% BTSE-incorporated coating, only slight amount of corrosion products appears around the defect. This suggests that the silane incorporation improves the corrosion protective properties of the electrophoretic coatings. The results of the SST are in good agreement with the conclusion derived from the EIS measurements.

Boiling water test, another simple and frequently used accelerated measurement, is used to evaluate the adhesion properties of the electrophoretic coatings. After immersion in boiling water for 6 h, big blisters are observed on the pure coating. But for silane-
incorporated coatings, only one or more small blisters or even no blisters are observed, depending on the silane type and its content. To quantitatively describe such distinct behaviors, EIS measurements in 3.5 wt.% NaCl solution are carried out after the boiling water test. The fresh samples (before the boiling test) all present very high impedance values ($\sim 10^{10} \Omega \text{ cm}^2$ when $f < 0.1 \text{ Hz}$), independent of silane modification (data not shown). As shown in Fig. 6, however, after boiling water test the low-frequency impedance of the blank specimen covered with pure electrophoretic coating drops more than 4 orders of magnitude, and the phase angle decreases dramatically at high frequency domain. Similar phenomenon can also be seen for the 0.5 wt.% MTMS-incorporated coating. But for 0.3 wt.% BTSE-incorporated coating, no obvious blister was observed after the boiling water test. The impedance of this sample drops less and still maintains at $\sim 10^7 \Omega \text{ cm}^2$ at low frequencies, indicating that BTSE provides much higher resistance against the expansion of active corrosion sites at metal/coating interface.

3.3. Physicochemical characterizations

The results of EIS during long-term immersion and the accelerated corrosion tests clearly indicate that the corrosion protective properties of the electrophoretic coatings are significantly improved by silane incorporation. Such positive role of silane component was already found in non-electrophoretic coating systems physically mixed [21,22] or chemically grafted [23,24] with organosilanes. Silanes had been considered [18–20,47], on the one hand, to enhance the cross linking of bulk polymeric structure by formation of chemical bonds between silane molecule and polymer backbone structure, and on the other hand, to strengthen the metal/coating interface by formation of silane-richened interfacial layer during the curing stage. In the present work, we believe that both the enhancement of crosslinking in the bulk coating and the formation of silane layer most likely occur in situ during the preparation step of electrophoretic coatings. The alkaline condition near the substrate and in the pores of paint during the electrophoresis facilitates the sol-gel process of silane agents. The physicochemical characterization results shown below clearly demonstrate the enhanced bulk coating structure and the improved metal/coating interface in the presence of silane.

The enhanced crosslinking of the bulk polymeric coating is supported by the reduced water uptake and the decreased water diffusion coefficient in the silane-incorporated coatings (Fig. 5). Such enhancement is expected to strengthen the mechanical property of the obtained polymer coatings. Fig. 7 shows the hardness and
Young's modulus of the electrophoretic coatings as a function of silane content. As shown in the figure, the hardness of the electrophoretic coating increases and then slightly decreases when the silane content increases, reaching the highlands at 0.3 wt.% BTSE and 0.5 wt.% MTMS, respectively. The hardness of MTMS-incorporated coatings is always bigger than that of BTSE-incorporated coatings, probably because of the more flexible structure of BTSE. Young's modulus goes similar results in hardness, i.e. first increases and then decreases with the increasing of silane content. The deteriorated performance in mechanical and anti-corrosive properties at excessive amount of silane incorporation can be explained by the existence of residual silane components in the coatings. Such residual silane components that are not crosslinked with the polymeric resin result in lower strength and less corrosion performance of the coating.

The enhancement in the bulk structure of silane-incorporated electrophoretic coatings can also be shown by the measurement of glass transition temperature (Tg). It was generally believed that water permeation into organic coating leads to the decrease in Tg since the adsorbed water can disturb the hydrogen bonds between the interchain [48]. Thereby, the variation of Tg during the service indicates the degree of polymer system plasticization and water/resin interactions [48]. Tg of the pure, BTSE and MTMS- incorporated electrophoretic coatings before and after exposure to 3.5 wt.% NaCl for a period of time are listed in Table 1. After incorporation of silanes, Tg (52.7 and 50.2 °C for MTMS and BTSE-involved coatings, respectively) decreases compared with that of the pure coating (58.6 °C). Similar phenomenon was also observed for polysiloxane-incorporated epoxy polymers [50]. This is caused by the standing of flexible structure coming from silane molecules. Nevertheless, we care more about the changes of Tg. As shown in the Table, for pure electrophoretic coating, Tg decreases drastically from 58.6 °C (fresh sample) to 44.3 °C after immersion for 42 days. Similar big decline of Tg for pure organic coating was also reported by us [41,51] and other researchers [52]. However, for MTMS and BTSE-incorporated coatings, only small decrease in Tg was observed after immersion (from 52.7 to 49 °C for the former, and from 50.2 to 44 °C for the latter). This indicates that silane incorporation weaken the detrimental effect caused by the permeated water and other corrosive species on the coating.

The silane incorporation is also found to increase the hydophobicity of the electrophoretic coatings, Fig. 8 shows that the water contact angle of the coating increases constantly when the silane...
content increases to 0.3 wt.%, and then the increase rate slows down, except for the abnormally high value at 1.0 wt.% MTMS. If considering much higher contact angle of pure BTSE film measured on aluminium substrate, ~92–94° [15,53], the improved contact angle of the silane-incorporated electrophoretic coatings (e.g. ~53° at 0.3 wt.% BTSE) is more likely caused by the enhanced bulk structure of polymeric coatings and is not originated from the silane component itself.

The mechanical measurement and results of $T_g$ changes and hydrophobicity all suggest that the silane incorporation enhance the bulk structure of the polymeric coatings. Such enhancement in the bulk structure provides good barrier properties (e.g. low level of water uptake and high resistance against ion penetration) which are the essentials for good corrosion performance. It is worth noting that the increased hydrophobicity of the primer layer would usually weaken the adhesion to the topcoat. However, thanks to the unique credit of organosilane compound in which the functional group could possibly be chemically coupled with the topcoat if proper combination between silane and topcoat is selected (e.g. the combined use of amino-grouped silane in the primer and the epoxy-grouped topcoat), one could easily overcome the above-noted problem. Actually, a two-layer “silane film/organic coating” painting system has been extensively investigated [16,54,55].

On the other hand, the strengthening of the metal/coating interface in silane-incorporated electrophoretic coating system is supported by boiling water test (Fig. 6), demonstrating that the adhesion between the substrate and the coating is obviously enhanced. In order to further investigate the mechanism for the improved adhesion properties, ATR-FTIR was carried out to measure the interfacial chemical information of the coatings. Fig. 9 displays the IR spectra of the 3.0 wt.% BTSE-incorporated coatings prepared by different electrophoresis times, representing the different coating thickness. The absorptions at 1501 and 1227 cm$^{-1}$, attributed to the substituted aromatic rings in epoxy resin and the ether bonds in epoxide groups [23], respectively, both slightly increase when the electrophoresis time increases, indicating the growing formation of epoxy coatings. It is surprising, however, that the intensity of

Table 1

<table>
<thead>
<tr>
<th>Electrophoretic coatings</th>
<th>Before immersion (°C)</th>
<th>After immersion (°C)</th>
<th>$\Delta T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>58.6</td>
<td>44.3</td>
<td>-14.3</td>
</tr>
<tr>
<td>0.3 wt.%BTSE</td>
<td>50.2</td>
<td>44.0</td>
<td>-6.2</td>
</tr>
<tr>
<td>0.5 wt.%MTMS</td>
<td>52.7</td>
<td>40.0</td>
<td>-12.7</td>
</tr>
</tbody>
</table>

* Samples of blank and 0.3 wt.% BTSE-incorporated coatings were immersed in 3.5 wt.% NaCl solution for 42 days, while the 0.5 wt.% MTMS-incorporated coating was immersed for 26 days.
absorption bands associated with the silane components, such as that at 799 cm⁻¹ (Si–C stretching) and that at 1080 cm⁻¹ (Si–O asymmetric stretching in Si–O–Si and Si–O–Metal [56]), declines with increasing electrophoresis time. One reasonable explanation is that the silane component is preferentially enriched at the metal/coating interface during the cathodic electrophoresis process by the formation of covalent bonds between silanes and the hydroxylated metallic substrate (Reaction (2b)). This causes the higher intensity of silane-related component for a thinner film. The silane enrichment leads to the formation of a dense and hydrophobic interfacial layer. Such interfacial layer provides an improved adhesion between the substrate and the electrophoretic coating, and also presents a high resistance against the corrosive attack. It is expected that under the cathodic conditions, the formation of silane interfacial layer becomes much easier.

4. Conclusions

We report here one-step electrochemical construction of silane-incorporated electrophoretic epoxy coatings. Both the EIS measurements during long-term immersion and SST suggest that the incorporation of appropriate amounts of silane agents significantly improves the corrosion performance of the electrophoretic coatings. The silane incorporation is found to enhance the bulk structure of the polymeric coatings, which leads to strengthening their mechanical properties, improving their hydrophobicity and slowing down the decrease of \( T_r \). In addition, silane incorporation is also found to strengthen the interfacial structure between the substrate and electrophoretic coatings by preferential formation of silane-enriched layer during the electrophoresis process. The structural enhancements both in the bulk coatings and in the metal/coating interface improve the barrier and the adhesion properties of silane-incorporated electrophoretic coatings. These explain their improved corrosion performance.

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