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# Enhanced corrosion resistance for silsesquioxane coatings by diglycidyl ether of biphenol A

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Based on silsesquioxanes (SSO), derived from hydrolytic condensation of (γ–glycidoxylpropyl)-trimethoxysilane (GPMS) and various amounts of tetraethoxysilane (TEOS), hybrid films (f-GST) were prepared using the sol-gel process. Because the epoxy-ring opening or the silica chains were not fully cross-linked, the f-GST was more susceptible to corrosion due to higher hydroxyl content and its hydrophilicity. Diglycidyl ether of biphenol A (DGEBA) was added into the reaction system to enhance the density of the film and to prevent epoxy ring opening during condensation. The film prepared with DGEBA, GPMS-SSO (GS) and 20 wt. % TEOS (f-GSTD) exhibited the best corrosion resistance compared with f-GST and bare aluminum alloy (AA). The f-GST and f-GSTD were studied as anticorrosion coatings on AA by electrochemical measurement. The results clearly demonstrate that samples with higher TEOS fractions have better anticorrosive performance and DGEBA obviously enhances the anticorrosion effect of f-GST.

Key words: *silsesquioxane; sol-gel; coatings; anticorrosion; electrochemical measurement*

## 1. Introduction

Silsesquioxane (SSO) compounds play an important role in coating film applications. These attractive engineering materials provide new opportunities to incorporate and release corrosion inhibitors due to their properties [1, 2]. In the early 1950s, Brady's group [3] at Dow Corning produced SSO copolymers (phenylsilsesquioxane-alkylsilsesquioxane) which were of low molecular weight but with high hydroxyl functionality on superstructures for corrosion protection of naval aircraft coatings. Du et al. [1, 4, 5] examined epoxy-SSO hybrid coatings on aluminum alloy (AA) substrates for corrosion protection using wet adhesion testing and electrochemical analy-

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ses. However, epoxy rings open in the hydrolytic condensation of GPMS, which may result in an incomplete crosslinked network and cracks in the film allowing water to be absorbed to the metal surface where corrosion occurs. Schmidt [6] found that controlled ring-opening reactions increased wettability, and diol crosslinking was found to improve corrosion resistance.

In the previous study, we reported the synthesis and characterization of SSO obtained from the hydrolytic condensations of (3-glycidoxypropyl)trimethoxysilane (GPMS-SSO, GS), with spectroscopic techniques (FTIR, NMR and UV-MALDITOF MS) [7, 8]. Properties (hardness, modulus, scratch, and abrasion) of the GS films (f-GSs) were measured with nanoindentation and nanoscratch techniques [9]. In this work, f-GSs are investigated as anticorrosion coatings on AA. Diglycidyl ether of biphenol A (DGEBA) and tetraethoxysilane (TEOS) are added to the reaction system to enhance the density of the f-GS and to prevent epoxy ring opening during condensation. The modified films act as corrosion inhibitors and enhance corrosion resistance.

## 2. Experimental

*Reagents.* Commercial (3-glycidoxypropyl)trimethoxysilane (GPMS, Sigma G 1535) was used in the examination of hydrolytic condensation reactions; diglycidyl ether of biphenol A (DGEBA) and tetraethoxysilane (TEOS) were employed as modifiers; formic acid (HCOOH, 98%), an analytical grade reagent, was used as a catalyst, ethanol ($C_2H_5OH$, 99.7 %) was used as a solvent, and ethylenediamine (EDA), an analytical grade reagent, was the hardener.

*GPMS-TEOS SSO*. The hydrolytic condensation of GPMS with different fractions of TEOS (0, 5, 10, 15, 20, 25 and 30 wt. %) was carried out in beakers placed in a water bath using HCOOH in the molar ratio HCOOH/Si = 3. The reaction was performed in three stages: plastic films were used to seal the beakers for 3 days (1); then several small needle-sized holes were made on the films before the reaction continued for another 3 days (2); and, finally, the film was removed and the reaction was continued for 4 days (3). The temperature at every stage was maintained at 35 ºC. The TEOS-modified SSO based on GPMS will be denoted as GST (GPMS–SSO–TEOS).

*GPMS–TEOS-DGEBA SSO.* To produce GPMS–TEOS-DGEBA SSO (GSTD), the same procedure as above was carried out with the fraction of TEOS 15 wt. %, and a the third stage DGEBA was added as a solvent (50% of the total number of epoxy groups were supplied by the solvent).

*SSO films.* The resulting SSO was diluted with ethanol (molar ratio Si/$C_2H_5OH$ = 1/4) and then a theoretical amount of EDA (molar ratio Si/EDA = 4/1) was added. Dip-coating on the AA LY12 (40×10×2 $mm^3$) was performed three times at 6-hour intervals with a dipping speed of 300 mm/min. After dipping, the coated samples were

put into a heating oven at 80 ºC for 6 hours, followed by 4 hours at 120 ºC. Coatings based on GST will be denoted as f-GST; f-GST with a different TEOS content will be denoted as f-$GST_{i\%}$ ($i$ = 0, 5, 15, 20, 25 and 30 wt. %); f-GSTD will be denoted as f-$GST_{10\%}$ containing 50 wt. % DGEBA modifier; and the AA coated with f-$GST_{i\%}$ will be denoted as AA–$GST_{i\%}$.

*Electrochemical test*. Electrochemical measurements were performed using an M 263A device (AMETEK) and a three-electrode cell equipped with a saturated calomel reference electrode (SCE), a platinum counter electrode, and a coated or non-coated AA panel as the working electrode with an exposed area of 1.0 $cm^2$. All measurements were conducted in an aqueous 3.5 wt. % NaCl working solution at room temperature. The electrodes were kept in the working solution for 30 min prior to measurements, with the electrical circuit opened. 352 SoftCorr III corrosion measurement software was used to analyze the potentiodynamic polarization curves. The potential scanning range was from –1 V to ca. 1.2 V with a scanning rate of 2 mV/s.

*Salt spray test.* Corrosion protection properties of the coated and non-coated AA substrates were evaluated by exposing the substrates to a salt spray atmosphere of 5 wt. % aqueous NaCl solution at 35 ºC. After removing from the salt fog chamber, all samples were rinsed with distilled water to remove any residues. Scanning electron microscopy (SEM) was performed on the bare and coated substrates to characterize the surface morphology before and after running the corrosion test.

## 3. Results and discussion

The anticorrosive performance of different sample coated films can be examined from the values of corrosion potential ($E_{corr}$) and corrosion current ($I_{corr}$). As listed in Table 1, the AA-GST shows a higher $E_{corr}$ and lower $I_{corr}$ than bare AA, but a lower $E_{corr}$ and higher $I_{corr}$ than the AA-$GST_{i\%}$ ($i$ = 5, 10, 15, 20, 25 and 30 wt. %). Figure 1 shows typical polarization curves of bare AA, AA-$GST_{10\%}$ and AA-GSTD. The polarization curves among AA-GST, AA-GSTD, and AA are different:

- The open circuit potentials of the AA-$GST_{10\%}$ and AA-GSTD are significantly higher than those of the bare AA.
- The rather lower current density of $6.02\times10^{-9}$ A/$cm^2$ results from the f-GSTD barrier that breaks down at a high electric potential and results in a failure of corrosion.
- The AA-$GST_{10\%}$ exhibits a different potentiodynamic polarization curve from AA-GSTD and AA and there is no obvious passivation region.

The $I_{corr}$ values of three samples are in the order of AA-GSTD<AA-$GST_{10\%}$<AA, which implies that the AA-GSTD and AA-$GST_{10\%}$ coatings indeed provide a physical barrier for blocking the electrochemical corrosion process. Current density initially increases rapidly, indicating an active electrochemical reaction. Furthermore, a rapid increase in electric potential results in the current density. For f-GSTD, a combination

of DGEBA, GS and 20 wt. % TEOS content produces hybrid materials with the best corrosion resistance properties. It is not prone to cracking during the curing period due to the slower speed used to produce homogeneous and dense coatings. This novel enhanced anticorrosion f-GSTD effect (as compared to the effect of f-GST) might have arisen from dispersing $SiO_2$ dense particles and organic fractions in a GSTD matrix to block the diffusion pathway of oxygen and water (see Figure 2). The previous study has evidenced the barrier effect of the PMMA-clay nanocomposites on $O_2$ and $H_2O$ molecules [10].

Table 1. Electrochemical parameters of bare AA and AA coated with films of various compositions

| Sample | Feed composition [wt. %] | | | Electrochemical parameter | |
|---|---|---|---|---|---|
| | GPMS | TEOS | DGEBA | $E_{corr}$ [mV] | $I_{corr}$ [nA/cm$^2$] |
| AA | 0 | 0 | 0 | –1016.0 | 5755.00 |
| AA-GS | 100 | 0 | 0 | –735.8 | 2089.00 |
| AA-GST$_{5\%}$ | 95 | 5 | 0 | –721.2 | 287.50 |
| AA-GST$_{10\%}$ | 90 | 10 | 0 | –713.4 | 173.50 |
| AA-GST$_{15\%}$ | 85 | 15 | 0 | –745.8 | 19.08 |
| AA-GST$_{20\%}$ | 80 | 20 | 0 | –725.0 | 12.42 |
| AA-GST$_{25\%}$ | 75 | 25 | 0 | –645.4 | 73.71 |
| AA-GST$_{30\%}$ | 70 | 30 | 0 | –696.7 | 55.14 |
| AA-GSTD | 40 | 10 | 50 | –595.5 | 6.02 |

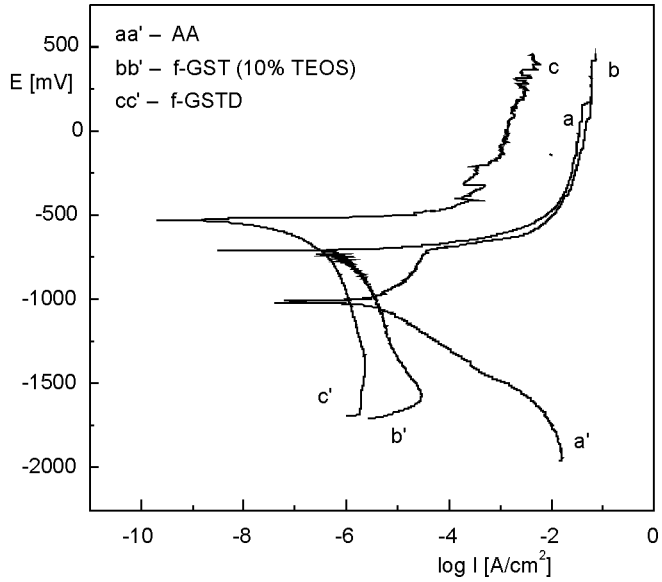


Fig. 1. Typical polarization curves of bare AA, AA-GST$_{10\%}$, and AA-GSTD. The data were for a 3.5 wt. % NaCl aqueous solution

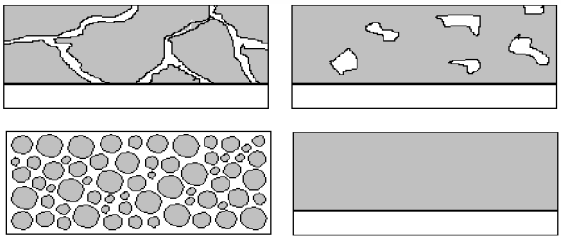

Fig. 2. Dispersion results of $SiO_2$ particles and organic fractions in a GTS matrix block (down) and the diffusion pathway of oxygen and water (up)

The SSO films and processing conditions strongly influence the anticorrosion properties of coatings. A sol-gel network based on linear silica chains would undergo an extensive cross-linking by hardener EDA leading to the formation of a dense coating. f-GST derived from the hydrolysis-condensation of GPMS, TEOS and EDA curing, unlike the f-GSTD coatings, produces relatively brittle films prone to cracking and degrades corrosion resistance. Although all six SSO films (f-$GST_{5–30\%}$) show significantly improved anticorrosion properties of coatings, there are obvious differences among those coatings (Table 1). AA-$GST_{20\%}$ shows better corrosion current due to an adequate amount of TEOS to fabricate a denser structure, and AA-GSTD shows the best anticorrosion properties as to corrosion current and corrosion potential. Previous studies have shown that GPMS is susceptible to ring opening reactions that form diol, alkoxy alcohol, and polyether products during the hydrolytic condensation [11–14]. Additional reaction products of the diol groups are possible in the presence of excess of alcohol and metal alkoxide leading to etherification or esterification between the OH groups and epoxy groups of DGEBA with the production of $–CH_2–CH(OH)–CH_2OR$ functionalities [15]. R may be $–CH_3$, $–C_2H_5$, $–SiO_{1.5}$ and $Si–(O_{0.5})_2R'$ units [16]. Polyether formation is also possible in GS films [17]. This additional reaction can make the crosslinking network denser and inhibit corrosion.

In the GSTD sol process, DGEBA was added into the GPMS system to control the ring-opening reaction. Williams et al. [18] found that the high stability of the GPMS -SSO/DGEBA solution and the epoxy rings of both GPMS and DGEBA were intact during the synthesis, which stemmed from the very low concentration of SiOH groups.

Figures 3a–c show the camera images of three samples after electrochemical measurements in 3.5 wt. % NaCl solution. Compared with the image of AA-GSTD, significant corrosion was found in both AA and AA-$GST_{20\%}$ but no obvious corrosion phenomena were found in the f-GSTD. Figure 3d-f shows the SEM images of the three samples after 282 hrs of salt spray tests. Although significant corrosion is found in all three samples, the extent of corrosion is appreciably different. The corrosion pits in the bare AA are much larger than in the coated AA. The corrosion area of AA-$GST_{20\%}$ is larger than the corrosion area of AA-GSTD. Obvious cracking and delamination phenomena are observed in the AA-$GST_{20\%}$ surface but are absent in the AA-GSTD surface. Trends of salt spray corrosion are similar to electrochemical corrosion.

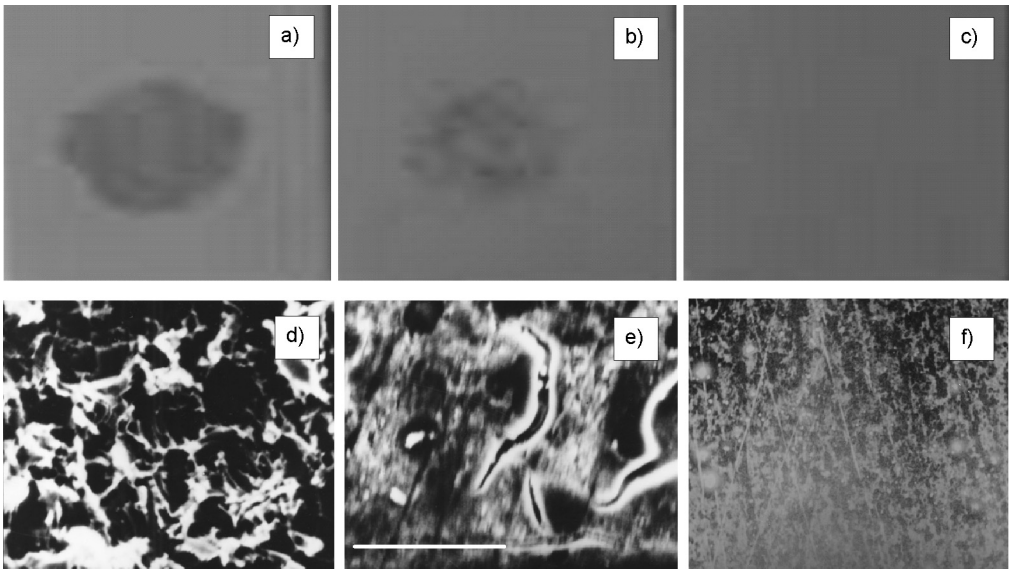


Fig. 3. Camera images (a–c) after electrochemical measurements in a 3.5 wt. % NaCl solution and SEM images (d–f), 800×, 15 kV, 100 μm, after salt spray tests at 282 hour for three samples: (a, d) AA, (b, e) AA-$GST_{20\%}$ and (c, f) AA-GSTD

## 4. Conclusions

Because the epoxy-ring opening or cross-linkng of silica chains was incomplete, the GPMS-POSS film was more susceptible to corrosion due to the higher hydroxyl content and its hydrophilicity. The f-GSTD prepared with DGEBA, GS and 20 wt. % TEOS exhibited the best corrosion resistance compared with the f-GST and bare AA. The results clearly demonstrate that the sample with higher TEOS fractions had better anticorrosive performance and DGEBA obviously enhances the anticorrosion effect of f-GST.

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