

# Corrosion protection of carbon steel by different alkoxysilanes via sol–gel method

Yu-Hsuen Lee<sup>a</sup>, Yu-Fong Yang<sup>a</sup>, Huey-Chuen I. Kao<sup>\*a</sup>, Chi-Fong Wu<sup>b</sup>, Wayne Tu<sup>b</sup> and Wen-Chang Liaw<sup>c</sup>

<sup>a</sup>Department of Chemistry, Tamkang University, Tamsui, Taiwan

<sup>b</sup>ED-TECH Co., Ltd., Taipei, Taiwan

<sup>c</sup>Department of Chemical and Material Engineering, National Yunlin University of Science and Technology, Douliou, Taiwan

## Abstract

Four alkoxysilanes, such as TEOS (tetraethoxysilane), TMOS (tetramethoxysilane), VTrMOS (vinyltrimethoxysilane), and APTreOS (3-aminopropyltriethoxysilane) were employed for making protective films on a carbon steel SAE 1018 substrate via sol–gel method. The sol–gel solution was prepared by mixing aniline, PMMA and alkoxysilane in NMP (N-methyl-2-pyrrolidone) at room temperature and reacting for several days. Followed by dip coating and thermal treatment, the film formed on the cleaned substrate is examined under the salt spray test in 5% sodium chloride aqueous solution. The corrosion resistance effect decreases in the order: TEOS > TMOS > VTrMOS > APTreOS. Films prepared by the TEOS sustain in the 5% saline solution for more than  $6(2) \times 10^2$  h.

**Keywords:** corrosion protection, SAE 1018 steel plate, salt spray test, sol–gel, organic–inorganic hybrid

Corresponding author: Huey-Chuen I. Kao

E-mail: kaohci@mail.tku.edu.tw

## Introduction

It is important to realize that corrosive attack on a metal can only occur at the surface, hence any modification of the metal surface or its environment can change the rate of reaction. A number of such methods have been developed, such as, surface coatings, electroplating, anodizing, galvanizing and the production of corrosion resistant alloys. Surface coatings using chemicals or mechanical means to place a protective layer between the materials and the corrosive environment from being eroded is the most commonly used methods. Coating materials commonly applied by the chemical vapor deposition (CVD), sputtering, electroplating and sol-gel method [1]. Sol-gel method of composite materials has the following advantages: (1) the processing temperature is generally low, frequently close to room temperature; (2) liquid precursors are used, it is possible to cast coatings in complex shapes and to produce thin films without the need for machining or melting; (3) an atomic scale mixing of non-ordinary physical blending, it is not easy to produce the phenomenon of phase separation; (4) through distillation and recrystallization, both starting chemicals and the products have high purity [1–3].

Wilkes *et al.* [4] reported hybrid materials termed ‘Ceramers’ which had been prepared by the incorporation of silanol-terminated poly(dimethylsiloxane) (PDMS) into a siloxane network derived from tetraethoxysilane (TEOS). These hybrids include only a siloxane network as an inorganic component. The TEOS–PDMS hybrids have been intensively studied and it has become clear that the structure and mechanical properties of the hybrids are strongly influenced by the processing conditions such as acid content, TEOS content and molecular mass of the PDMS. Mackenzie *et al.* [5] reported the PDMS–SiO<sub>2</sub> organic–inorganic hybrid materials by sol–gel method. When a polymer such as silanol terminated polydimethylsiloxane (PDMS) is mixed with TEOS in a suitable solvent and catalyst, gels can be prepared which exhibit rubbery elasticity. The microstructures of such organically modified silicates (ormosils) can be controlled to give solids which are opaque or transparent via experimental variables. Nakata *et al.* [6] reported the PDMS–polyamide–SiO<sub>2</sub> hybrid materials by sol–gel method, they found that raising temperature could shorten the gel formation time and increased the content of SiO<sub>2</sub>. The composite is hard and transparent.

In the study of the reaction between the organic polymer PVP (poly(alkyloxazoline)-vinyl polymer) containing an N-alkylamide group and TEOS, Saegusa *et al.* [7] assumed a molecular-level dispersion of the polymer in the framework of silica gel, which was due to the hydrogen-bond interaction between the PVP and silanol group of silica gel. The composite was stable at room temperature and pH 5.0, as long as for 10 days. Saegusa [8] proposed the theory of organic–inorganic hybrid materials, dimension of dispersion of ‘hybrids’ was much smaller than that of the so-called ‘composites’. The most suitable organic polymers for the formation of hybrids are those which consist of repeating unit containing

N-alkyl and N, N-dialkyl carboxylamide groups ‘amide polymers’. Two types of interactions between organic polymer and silica have successfully been adopted in order to avoid the phase separation to produce homogeneous transparent materials. The first one is the formation of covalent bond between organic polymer and silica. The second type is the formation of hydrogen bond between silanol group of the intermediate species from Si(OR), and the basic group of the hydrogen acceptor function in organic polymer. The third type is based on the combination of the above two types of interaction.

Chen *et al.* [9] prepared a high-refractive-index trialkoxysilane-capped PMMA-titania hybrid optical thin films by an in situ sol-gel process, followed by spin-coating and multistep baking. The prepared hybrid films show potential applications in optical devices, which exhibit very high optical transpance in the visible region. Chou *et al.* [10] copolymerized tetraethoxysilane and 3-methacryloxypropyl trimethoxysilane (MPS) with a two-step acid catalyst process to form the hybrid sols. Hybrid coatings on stainless steel substrates demonstrated the corrosion protection by forming a physical barrier. Sugama [11] made hybrid coatings to protect steel and aluminum against corrosion by adding about 20 wt.% of Ce acetate as corrosion inhibitor into 3-aminopropyl trimethoxysilane (APS) sol. Duran and coworkers [12] used TEOS and MTES (methyltriethoxysilane) to form a thick hybrid sol-gel coating under basic catalyst and found that the corrosion mechanisms for sol-gel galvanized steels did not change with respect to the uncoated steel. The sol-gel coating provided good protection for the zinc coating underneath and steel substrate at the same time.

In this study, we adopt the concept of organic-inorganic hybrid materials to prepare protective films on the SAE 1018 steel plates via sol-gel method by using different alkoxyxilanes, PMMA and aniline. The salt spray test was employed for the corrosion resistance examination.

## Experimental

Four alkoxyxilanes, including 99% pure TMOS and APTreOS, 98% pure TEOS, and VTrMOS were purchased from Acros. 99% pure NMP (N-methyl-2-pyrrolidone), aniline from Junsei Chemical and PMMA (polymethyl-methacrylate, average MW is 350,000 g/mol) from Aldrich. Aniline was distilled before using. Sol-gel solution was prepared by the following procedures. Fixed amount of aniline and NMP were mixed and stirred for 1 h in an Erlenmeyer flask. NMP was used as solvent for the reaction. Alkoxyxilanes, such as TEOS, TMOS, VTrMOS or APTreOS was added and stirred for 1 d. Then, 2.50 g of PMMA was mixed and completely dissolved in the above solution, it took about 4 d. Mole ratio of aniline : NMP : alkoxyxilane = 0.068 : 0.250 : 0.010. All the reactions were running at room temperature. Hydrolysis and polycondensation reactions of the alkoxyxilanes were followed by IR spectra and the viscosity of the solution in centipoises ( $cP = 0.001 \text{ N}\cdot\text{m}^{-2}\cdot\text{s} = 10^{-3} \text{ Pa}\cdot\text{s}$ ) was measured during the reaction. Infrared spectra were obtained using a Bio Rad FTIR

Spectrometer, model FPS 3000. The IR samples were prepared by adding sol–gel solution into dried KBr powder, thoroughly mixed and then pressed into thin pellets.

Steel plates from China Steel Corporation in Taiwan were cut into 20 mm x 30 mm x 3 mm specimens and stored in silicone oil before use. They were structural quality hot rolled SAE 1018 steel (minor compositions: 0.18 – 0.20% C; 0.60 – 0.90% Mn; < 0.030% P; < 0.050% S). Substrate was washed by n-hexane to remove the storage oil on the surface and then cleaned by an ultrasonic vibrator in acetone for 10 min. All sides of the substrate were polished using 100 grade emery papers to remove any residue or oxide covered on the surface. The substrates were sprayed by a solution containing 0.10 M citric acid and a proper amount of triethanolamine (TEA) to further de-rust the surface of the metal.

Cleaned substrate was dipped coated in the sol–gel solution and then heat treated at 120 °C for 24 h. They were characterized by the standard adhesion test [13], hardness test [14] and salt spray test [15]. Surface morphology of the film was examined on a Tescan VEGA\SBH scanning electron microscope.

## Results and Discussion

Viscosity of the sol–gel solution prepared by the TEOS, TMOS, VTrMOS and APTreOS when they were ready for coating is 50.3, 33.8, 29.4 and 63.7, respectively. Dip coated films have thickness of 7.2(2), 5.0(4), 2.7(3) and 9.7(4)  $\mu\text{m}$ . Thickness of the film is about linearly dependent on the viscosity of the solution, which is plotted in Fig. 1. The sol–gel solution was prepared by fixing the mole ratio of these four major constituents: aniline, NMP, PMMA and alkoxy silane. Although there was no water added to the solution, we deduce that the trace amount of water contained in the NMP provides the  $\text{H}_2\text{O}$  required for the hydrolysis of the alkoxy silanes.

Applying 1 kg force on the pencil, the hardness test found that all films are 9 H, the highest value can be obtained by this measurement. Under the adhesion tape test, all of them have  $\leq 5\%$  areas removed.

Fig. 2 and Fig. 3 show the absorbance of the IR spectra in the range of 850 – 1200  $\text{cm}^{-1}$  for the sol–gel solution after addition of TMOS and TEOS for 24 – 360 h. At 930 and 980  $\text{cm}^{-1}$ , they are the stretching vibration of the Si–OH [16] due to the hydrolysis of TMOS and TEOS with water. At 1150  $\text{cm}^{-1}$ , it is the vibration of Si–O–Si mode, which is a result of the polycondensation reaction [16]. All the absorptions at 930, 980 and 1150  $\text{cm}^{-1}$  increase with increasing the reaction time. After 24 h, the peaks at 930 and 980  $\text{cm}^{-1}$  are very small. After 48 h, they are clearly seen. They are still growing after 144 h of the reaction that is the evidence of the hydrolysis of TMOS and TEOS in the sol–gel solution. For the absorption peak at 1150  $\text{cm}^{-1}$ , after 24 h, this peak is small too. The peak grows gradually with

increasing the reaction time. These are the evidence of the hydrolysis and polycondensation reactions happened in the alkoxy silanes.

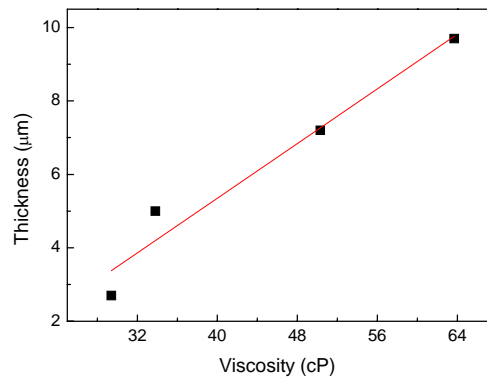


Fig. 1. Relationship between the viscosity and thickness of the dip coated films.

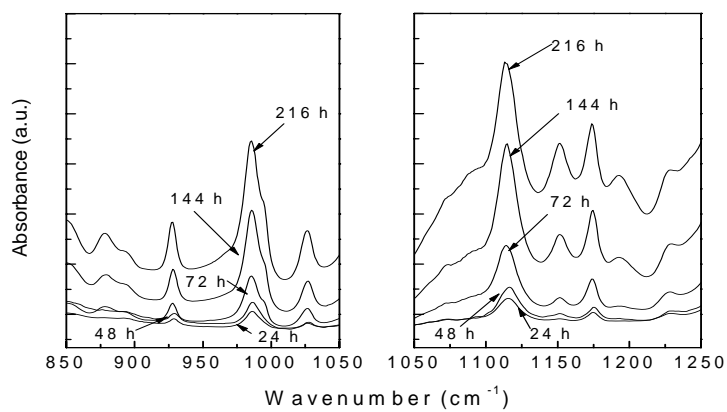


Fig. 2. IR spectra of the sol-gel solution prepared by TMOS after different reaction periods.

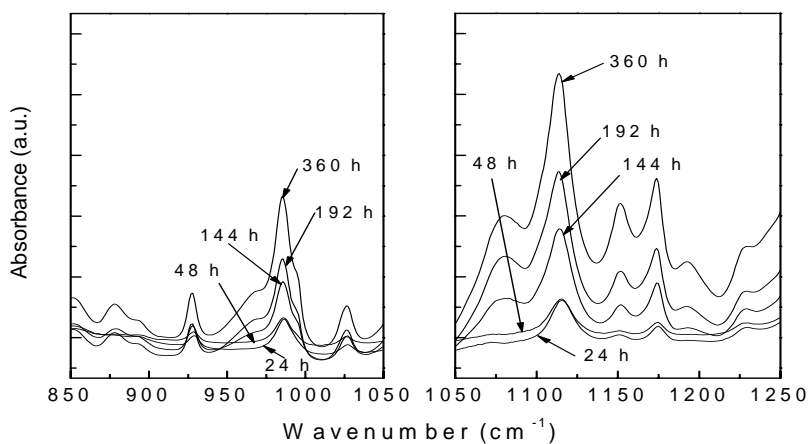


Fig. 3. IR spectra of the sol-gel solution prepared by TEOS after different reaction periods.

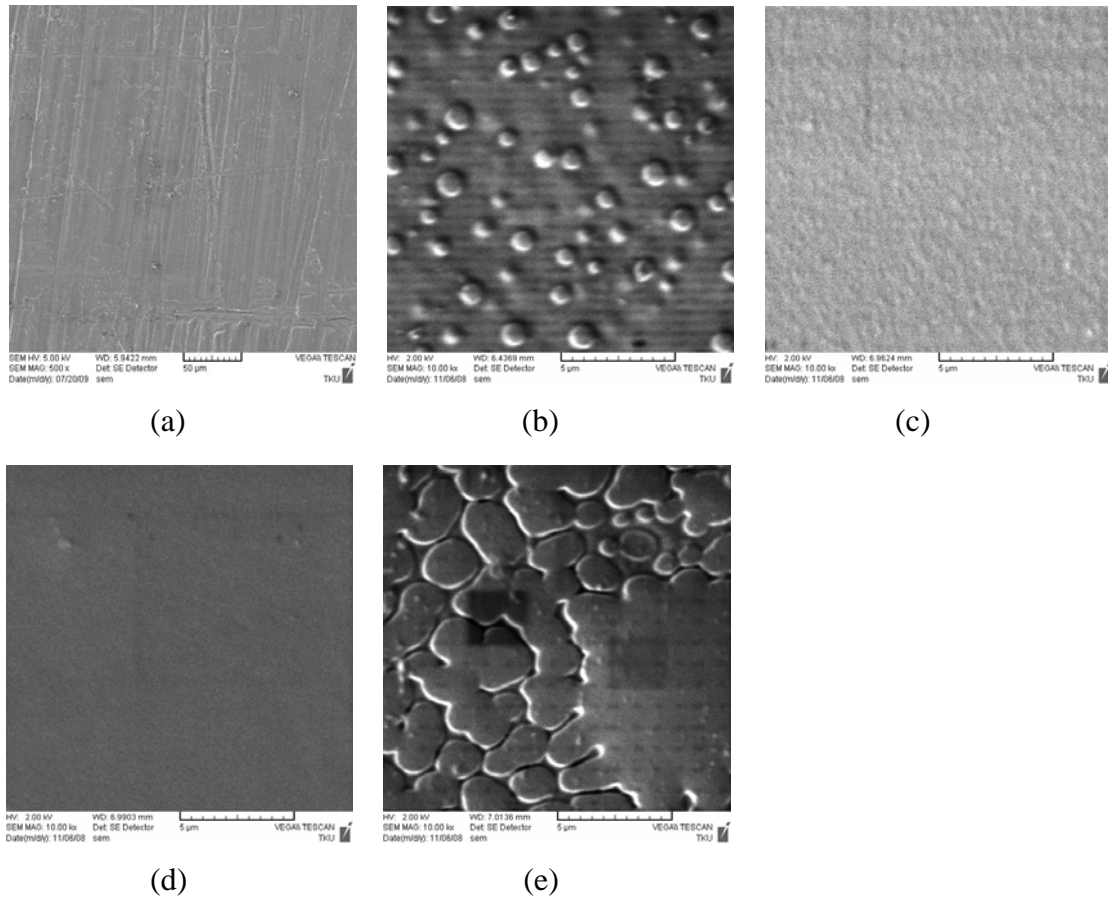


Fig. 4. Morphology of the films prepared by different alkoxy silanes: (a) uncoated steel, (b) TEOS, (c) TMOS, (d) VTrMOS, and (e) APTreOS under SEM by 10,000 magnifications.

Examination of the morphology of the coated films under SEM, the samples prepared by different alkoxy silanes is shown in Fig. 4, under 10,000 times magnification. In order for comparison, bare substrate is shown in Fig. 4(a), brushing trails are clearly viewed. Different morphology is observed among them. Many round shape particles with a diameter about 1  $\mu\text{m}$  are observed on the film prepared by TEOS. Rough surface is found on the surface prepared by the TMOS. Surface of the film prepared by the VTrMOS is quite smooth and that prepared by the APTreOS is much different from others. The film is discontinuous with a few small particles embedded.

In the 5% NaCl salt spray test (SST), the corrosion time is recorded when 15% surface areas are corroded. The corrosion time of the films prepared by TEOS, TMOS, VTrMOS, APTreOS and bare steel were 6(2), 3.8(9), 2.9(7), 0.7(3)  $\times 10^2$  h and 0.26 h, they are plotted in Fig. 5. For steel without coating, it only sustains in the salt spray mist for 0.26 h. Apparently, all of the films have the ability to protect steel from corrosion. Among them, TEOS is the best and TMOS is the second. It seems better to use the alkoxy silanes with four functional Si-OR groups as starting materials to make sol-gel solution. Both TEOS and

TMOS have four –OR groups, which allow Si atom to form three dimensional SiO<sub>2</sub> network in the polycondensation reaction. On the other hand, the other two alkoxy silanes have three Si–OR groups, only two dimensional networks of –SiO<sub>3</sub> are possibly formed. That is probably the reason why their protecting ability is decreased. The decreasing order of the protection by the films prepared with different alkoxy silanes is TEOS > TMOS > VTrMOS > APTreOS. Although the condensation products formed by both TEOS and TMOS are the same, comparing the corrosion protection of the film formed by the TEOS and TMOS, the former is better, which is probably governed by the thickness of the film. The former is 7.2 μm and the latter is 5.0 μm. The film prepared by the APTreOS only sustains in the SST for 69 h that is probably due to the discontinuous of the coated film shown in Fig. 4(e).

Comparing with other similar report, Rahman *et al.* [17] preparing two layers films by galvanostatically synthesized polypyrrole on carbon steel, and than an epoxy paint is applied on it, which has a thickness of 60 μm, the corrosion time of the film is 120 h under the SST that is shorter than the films prepared by TEOS, TMOS and VTrMOS. It seems that sol–gel and PMMA hybrids provide a better corrosion protection on the carbon steel plates.

## Conclusions

Four alkoxy silanes had been selected for making protective films on steel surface via a sol–gel method. All of them have corrosion resistance effect to some extent, hardness of the films is 9 H under 1 kg pencil test and they show relatively good adhesion with the metal substrate, only ≤ 5% areas are removed by the tape test. By the salt spray test, TEOS is the best alkoxy silane among them for preparing the protective film on steel surface. It seems that the alkoxy silanes with four functional groups are more effective in the corrosion protection of the steel substrates.

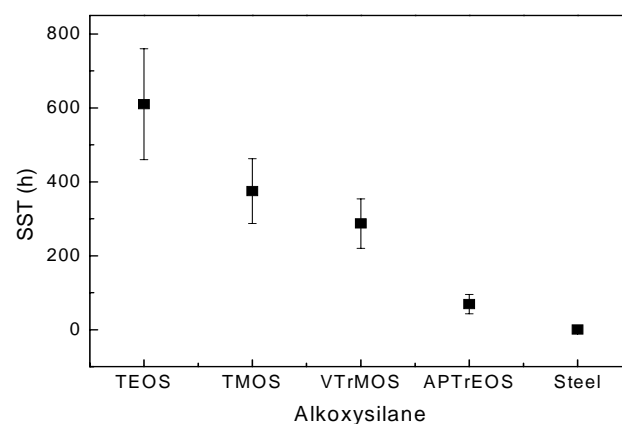


Fig. 5. SST results of the samples prepared by different alkoxy silanes while 15% areas were corroded by 5% NaCl solution mist.

## Acknowledgment

The authors would like to thank the ED-TECH Co., Ltd. for the financial support of this work. Steel plate obtained freely from China Steel Corporation in Taiwan is also thanks.

## References

- [1] Wang, D.; Bierwagen, G. P. *Prog. Org. Coat.* **2009**, *64*, 327.
- [2] C.J. Brinker, A.J. Hurd, P.R. Shunrk, *J. Non-Cryst. Solids* **1992**, *147* (1992) 424.
- [3] J.D.Wright, N.A.J. Sommerdijk, *Sol–Gel Materials Chemistry and Applications*, CRC Press, OPA Overseas Publishers Association, 2001.
- [4] Wilkes, G. L.; Orlor, B.; Huang, H. *Polym. Bull.* **1985**, *14*, 557.
- [7] Saequsa, T. *J. Macromol. Sci. Chem. A* , **1991**, *28*, 817.
- [5] Mackenzie, J. D.; Chung, Y. J.; Hu, Y. *J. Non-cryst. Solids*, **1992**, *147*, 271.
- [6] Nakata, S.; Kawata, M.; Kakimoto, M. A.; Imaj, Y. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 3425.
- [8] Saequsa, T. *Pure and Appl. Chem.* **1995**, *67*, 1965.
- [9] Lee, L. H.; Chen, W. C. *Chem. Mater.* **2001**, *13*.
- [10] Chou, T. P.; Chandrasekaran, C.; Cao, G. Z. *J. Sol–Gel Sci. Technol.* **2003**, *26*, 321.
- [11] Sugama, T. *J. Coat. Technol. Res.*, **2005**, *2* (October), 649.
- [12] Conde, A.; Damborenea, J. D.; Duran, A.; Menning, M. *J. Sol–Gel Sci. Technol.* **2006**, *37*, 79.
- [13] ASTM D3359, standard test methods for measuring adhesion tape test.
- [14] ASTM D3363, standard test methods for film hardness by 1 kg pencil test.
- [15] ASTM D1654, test method for evaluation of painted or coated specimens subjected to corrosive environments.
- [16] Mauritz, K. A. *Mater. Sci. Eng. C.* **1998**, *6*, 121.
- [17] Rahman, S. U.; Abul-Hamayel, M. A.; Abul-Aleem, B. J. *Surf. Coat. Technol.* **2006**, *200*, 2948.