

## Spectroscopic Studies of Epoxy Coated Steel (II)

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*Received July 11, 1994*

**ABSTRACT:** Various silane coupling agents have been introduced to protect the surface from corrosion of epoxy/steel system. Under the hot/wet condition, amino silane occurs the degradation and forms the surface corrosion on the steel. In the case of  $\gamma$ -MPS/steel system, the oxidation of steel surface was suppressed due to the improved adhesion of  $\gamma$ -MPS in humid environment. In epoxy/silane/steel system, chemical bonding at the silane/steel may improve the corrosion protection on the steel surface. In addition, the role of zinc powder has been evaluated in the epoxy/steel system through the cathodic protection mechanism.

### Introduction

When the metal is exposed to ambient environment, most of metals corrode through the charge transfer reaction which makes the deterioration of metals at the metal surface.<sup>1</sup> This metallic corrosion causes tremendous waste of limited natural resources.<sup>2</sup> National Bureau of Standards announced in 1978 that annual economic losses in U.S.A. had been estimated at \$120 billion due to the metal corrosion.<sup>3</sup>

Several researchers studied the steel corrosion under the hot/wet environment. Evans *et al.* reported that  $\text{Fe}_3\text{O}_4$  was air oxidized directly and formed ferrous rust in the atmospheric corrosion environment.<sup>4</sup> Keiser *et al.* studied the oxidation of  $\text{Fe}_3\text{O}_4$  on steel surface and they concluded that  $\text{Fe}_3\text{O}_4$  was oxidized initially to  $\alpha$ - $\text{FeOOH}$  under the severe environment.<sup>5</sup>

In order to protect the steel from corrosion, the proper corrosion inhibitors are strongly needed to extend the service life of steel. Recently, silane coupling agent was used for the corrosion protection and the adhesion promotion of organic coating/steel system.<sup>6–11</sup> Several studies have been undertaken to investigate the effectiveness of silanes for the chemical bonding of metals with structural adhesives.<sup>5–9</sup> They have been mostly concerned with the dry and wet strengths of metal lap shear or butt joints bonded with two-part epoxy system.

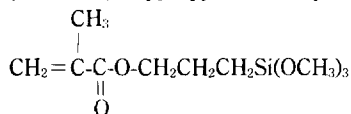
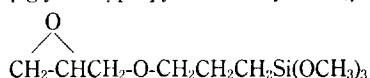
Thiedman *et al.* studied the performance of various organofunctional silane coupling agents as

adhesion promoters for epoxy-based structural film adhesives.<sup>12</sup> From the study of lap shear strength and durability, it was concluded that the epoxy silane was efficient adhesion promoter with film adhesive and the neutral silanes, which were methacrylate, chloropropyl, and vinyl triacetoxyl, were less effective. In the case of aminosilane, silane did not have a role of the adhesion promoter for epoxy film adhesives, whereas it should be chemically reactive in epoxy system.

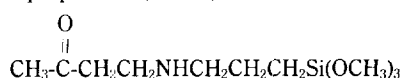
Leidhesier *et al.* studied the corrosion protection of steel pretreated with silanes.<sup>12</sup> Silane coupling agents were used by dry blending method for polybutadiene/steel system. From their results, it was concluded that Fe-O-Si bonds formed during silanization and the formation of hydrogen bonding at silane/steel interface enhanced the adhesion strength. It provided the good corrosion protection of steel substrate. Through the strong adhesion at both the substrate/silane and silane/coating interfaces, the silane treated system has the good delamination resistance of the organic coating system.

In a previous paper, we have discussed the spectroscopic studies of the epoxy and epoxy/DSO system on the steel surface.<sup>13</sup> Epoxy/DSO system provides the good film formation on the steel surface due to the reduced shrinkage of epoxy resin. Improved film property on the steel surface protects the corrosion formation on the steel surface more or less in the humidity chamber.

Present study is directed towards the use of silane coupling agent and zinc dust for the epoxy/steel system. The purpose of this paper is, there-

**Table I. Chemical Structure of Silanes in This Study**A)  $\gamma$ -methacryloxypropyltrimethoxysilane( $\gamma$ -MPS)B)  $\gamma$ -glycidoxypropyltrimethoxysilane( $\gamma$ -GPS)C)  $\gamma$ -aminopropyltrimethoxysilane( $\gamma$ -APS)

D) methyl(2-(3-trimethoxysilylpropylamino)ethylamino) 3-propionate (MPEP)



fore, to study the corrosion protection of steel surface using the various silane coupling agents. In addition, the role of zinc dust in epoxy/steel system has been investigated by Fourier Transform Infra-red Reflection-Absorption Spectroscopy (FTIR-RAS).

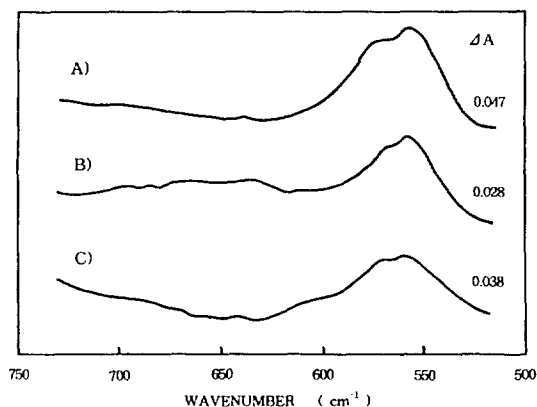
## Experimental

The silanes for this study were purchased from Petrarch Systems Inc., and were hydrolyzed for one hour in deionized water/tetrahydrofuran (THF) mixed solution. Chemical structures of various silanes in this study are listed in Table I.

The steel used is aluminum killed and batch annealed to provide a fine grain size. Steel specimens (2.5 cm  $\times$  5.0 cm) were mechanically polished, and final polish was carried out with 3  $\mu\text{m}$  diamond paste. Polished samples were ultrasonically washed in acetone. This was followed by repeated rinsing with methanol, blown with nitrogen gas and stored in the desiccator until use.

The epoxy resin (EPON 828) was supplied by Shell Chemical Co. Solution casting of the epoxy/chloroform solution was used to coat the steel. 10 phr  $\text{BF}_3$ -mono ethylamine (Anchor 1115) based on the amount of epoxy was applied as an curing agent.

Dinorbornene spiro orthocarbonate (DSO) was mixed with epoxy to reduce the shrinkage stress of epoxy through the ring opening polymerization. Recommended amount of antishrinking agent is 10



**Figure 1.** R-A Spectra of cured epoxy and epoxy/Zn system: A) Cured epoxy after humidity test, B) Cured epoxy/Zn, and C) The difference spectrum (A-B).

phr DSO based on the epoxy.

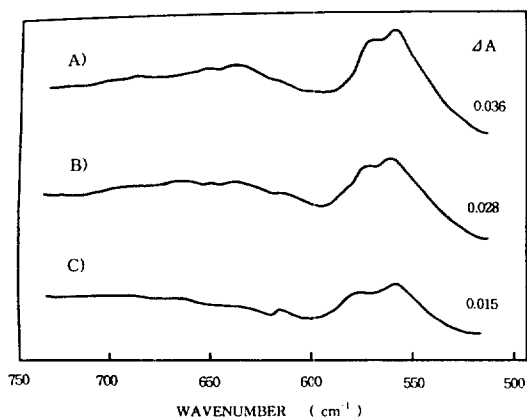
All epoxy coated samples were cured at 140  $^{\circ}\text{C}$  for 1 hr. Cured samples were then exposed in a 100% relative humidity chamber at 95  $^{\circ}\text{C}$  for 12 hr.

Zinc dust was mixed with epoxy resin and applied for the epoxy/steel system in order to provide the self-healing capacity for the pitting corrosion. FTIR-RAS technique was used for the analysis of coating films on steel. The reflection-absorption attachment (Harrick-Scientific) with a gold wire grid polarizer (Perkin-Elmer) was mounted on a Digilab FTS-14 spectrometer. The spectra were collected as the average of 200 scans at 4  $\text{cm}^{-1}$  resolution. The angle of incidence was 75 $^{\circ}$  for this study. The spectra of the coating samples were subtracted from the reference spectrum of bare steel.

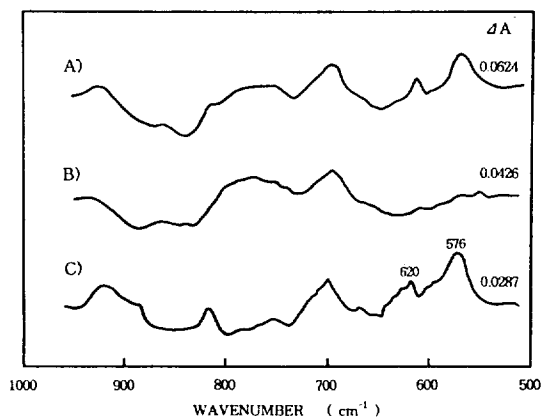
## Results and Discussion

Figure 1 represents the R-A spectra of the epoxy/steel and epoxy/Zn/steel system under the hot/wet condition. The spectrum of the cured epoxy on the steel is shown in Figure 1A, and that of epoxy/steel with zinc system in figure 1B. Film thickness of epoxy resin is fixed to 1.0  $\mu\text{m}$ . Epoxy/steel with zinc system provides less formation of  $\text{Fe}_3\text{O}_4$  compared to the epoxy/steel system. From the difference spectrum, it has been observed that epoxy with zinc system shows less corrosion formation compared to the epoxy system. Zinc powder lowers the open circuit potential of steel below its critical corrosion potential through the cathodic protection mechanism.

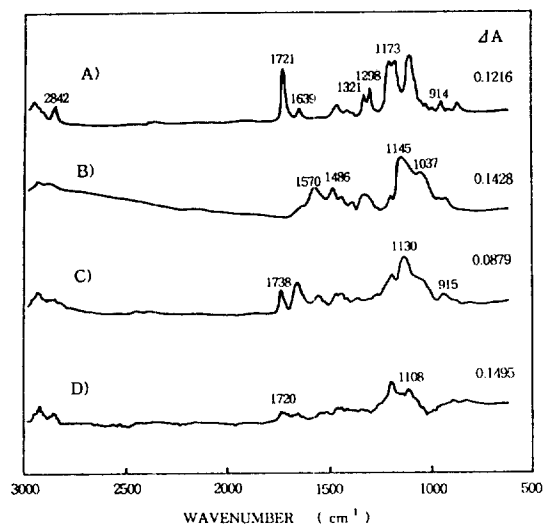
Figure 2 indicates the effect of thickness in



**Figure 2.** R-A Spectra of cured epoxy/Zn system with different thickness: A) 0.5  $\mu\text{m}$ , B) 1.0  $\mu\text{m}$ , and C) the difference spectrum (A-B).



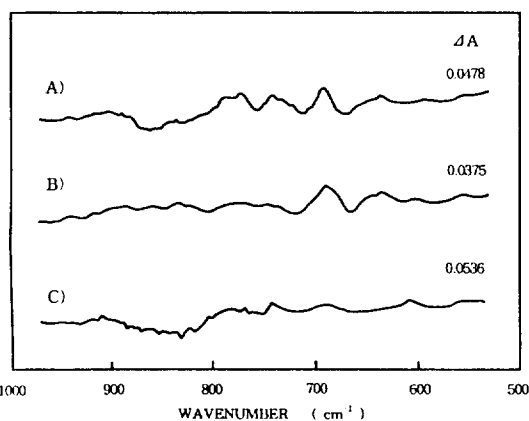
**Figure 4.** R-A Spectra of  $\gamma$ -APS coated steel: A) After humidity test, B) Before humidity test, and C) The difference spectrum (A-B).



**Figure 3.** R-A Spectra of various silanes on the steel surface: A)  $\gamma$ -MPS, B)  $\gamma$ -APS, C)  $\gamma$ -GPS, and D) MPEP.

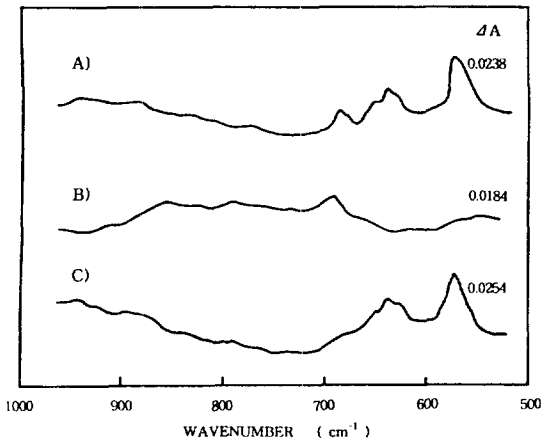
epoxy/steel system with zinc powder. After the hot/wet test, this system effectively suppresses the corrosion formation of the steel surface. The difference spectrum indicates that the epoxy thickness also affects the protection of the steel corrosion. Judging from these data, zinc powder and the thick coated epoxy resin on the steel surface improve the prevention of steel corrosion.

Figure 3 shows the R-A spectra of various silane coupling agents on steel. The spectrum of  $\gamma$ -MPS is represented by Figure 3A. The band at  $1721\text{ cm}^{-1}$  is assigned to the C=O group and the C=C stret-

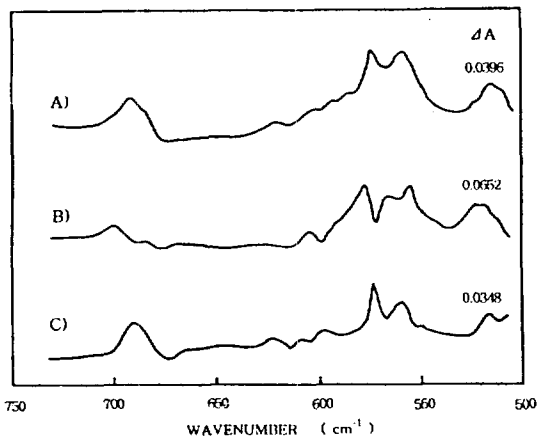


**Figure 5.** R-A Spectra of  $\gamma$ -MPS coated steel: A) After humidity test, B) Before humidity test, and C) The difference spectrum (A-B).

ching mode appears at  $1639\text{ cm}^{-1}$ . The band at  $914\text{ cm}^{-1}$  originates from the vinyl wagging vibration. The peak at  $2842\text{ cm}^{-1}$  is due to the C-H stretching of the Si-CH<sub>2</sub> group. The peaks at  $1321\text{ cm}^{-1}$ ,  $1298\text{ cm}^{-1}$ , and  $1173\text{ cm}^{-1}$  are associated with the ester functionality. From the R-A spectrum of  $\gamma$ -APS shown by figure 3B, the peaks at  $1570$  and  $1486\text{ cm}^{-1}$  are attributed to the deformation modes of amine bicarbonate and the splittings of  $1145\text{ cm}^{-1}$  and  $1037\text{ cm}^{-1}$  indicate the silanol condensation of  $\gamma$ -APS molecules. The spectrum of  $\gamma$ -GPS is shown by Figure 3C. The band at  $1130\text{ cm}^{-1}$  is strongly influenced by the degree of crosslinking of the siloxanes and the band at  $915\text{ cm}^{-1}$  is assigned to the terminal epoxy ring. The band intensity of the ester



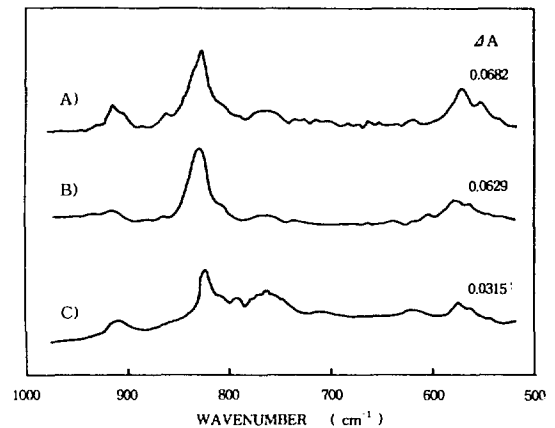
**Figure 6.** R-A Spectra of  $\gamma$ -GPS coated steel: A) After humidity test, B) Before humidity test, and C) The difference spectrum (A-B).



**Figure 7.** R-A Spectra of MPEP coated steel: A) After humidity test, B) Before humidity test, and C) The difference spectrum (A-B).

group at  $1738\text{ cm}^{-1}$  increases as the cure reaction proceeds. In the case of MPEP (Figure 3D), the stretching band at  $1108\text{ cm}^{-1}$  is attributed to the C-O-C asymmetric stretching mode in the aryl ester and C=O stretching mode appears at  $1720\text{ cm}^{-1}$ .

Figures 4, 5, 6, and 7 represent the R-A spectra of various silanes on the steel surface before and after hot/wet test. This test was carried out at  $95^\circ\text{C}$ , for 12 hr in the 100% relative humidity chamber. From the Figure 4, the R-A spectrum of hot/wet treated  $\gamma$ -APS indicates the oxide formation on steel surface, whereas untreated silane coated steel does not have the corrosion of steel. The band at  $576\text{ cm}^{-1}$  is attributed to  $\text{Fe}_3\text{O}_4$  and the peak



**Figure 8.** R-A Spectra of silane/epoxy with zinc powder on the steel: A) silane/epoxy coated steel, B) silane/epoxy with zinc on the steel, and C) the difference spectrum.

of  $\alpha\text{-FeOOH}$  appears at  $620\text{ cm}^{-1}$ . The difference spectrum of  $\gamma$ -APS coated steel demonstrates the formation of a large amount of  $\text{Fe}_3\text{O}_4$  on steel surface after hot/wet test.

In Figure 5, the coated methacrylate silane suppresses the oxide formation of steel surface under the severe condition. The absorbance at  $822\text{ cm}^{-1}$  reduced due to the decrease of the Si-OCH<sub>3</sub> groups after hydrolysis. Hydrolyzed silane can react with the hydroxyl group of steel surface and a chemical linkage, which results in a Fe-O-Si bond, occurs through the condensation.

In Figure 6,  $\gamma$ -GPS is also tested by the hot/wet condition and the difference spectrum of  $\gamma$ -GPS represents a large amount of  $\text{Fe}_3\text{O}_4$  and a small amount of  $\alpha\text{-FeOOH}$  formation. In this case, the epoxy functional group of  $\gamma$ -GPS does not work for the corrosion protection effectively.

On the other hand, MPEP has the acetoxy functional and amine functional group. After hot/wet treatment, the R-A spectrum of MPEP/steel is shown by Figure 7. It indicates that  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-FeOOH}$  form on the steel surface after hot/wet test. Compared to the  $\gamma$ -APS, the degree of corrosion on steel is lowered due to the hydrogen bonding of the acetoxy functional group. Judging from these data, it can be concluded that the acetoxy functional silane has the good corrosion barrier for the steel surface under the severe condition.

The effect of zinc powder in epoxy/ $\gamma$ -APS/steel system is demonstrated by Figure 8. The thickness of silane/epoxy is fixed to  $1.0\text{ }\mu\text{m}$ . Two weight per-

cent of zinc powder is mixed with epoxy resin and applied to the steel surface.

From the previous results, epoxy coated silane/steel systems hinder the corrosion formation on steel surface, but they still form the oxide film on the steel surface. The degree of oxidation on the steel surface is strongly dependent on the functional group in the silane coupling agent. Zinc powder has the role of corrosion protection for the steel surface through a cathodic protection mechanism. Zinc metal acts as an effective heavy metal ion scavenger in aqueous solution.<sup>13-16</sup> Steel corrosion protection by zinc powder can be explained mostly through the cathodic protection process from the pitting corrosion, wherein zinc powder contacting the steel surface lowers the open circuit potential of the steel to below its critical pitting potential.

In the case of  $\gamma$ -APS, the difference spectrum suggests that zinc powder is very effective for the decrease of open circuit potential through the cathodic reaction and for the corrosion retardation on the steel surface. Zinc dust has the good capability to suppress the corrosion formation under the severe service environment.

## Conclusion

Reflection absorption spectroscopy(RAS) has been used for the characterization of silane coupling agents in epoxy/steel system. In silane coated steel system,  $\gamma$ -MPS has the capability to suppress the oxidation on the steel surface in humid condition. Under the hot/wet condition, aminosilane coated steel forms the oxidized film through the degradation and the delamination of silane at the epoxy/steel interface.

In epoxy/silane/steel systems, chemical linkages at both the silane/coating and the silane/substrate interfaces may affect the corrosion protection on the steel surface. The coating systems with zinc dust have the good corrosion protection under the

severe environment. Through the cathodic protection mechanism for the steel surface, zinc powder lowers the open circuit potential of steel below its critical corrosion potential.

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