

Chapter 4

THIOL-MODIFIED RESIN COATED ON GALVANIZED STEEL SHEETS

4.1 INTRODUCTION

Metals that are typically exposed to environmental conditions for prolonged periods of time require a protective coating to protect the exposed surface from corrosion. A common protective coating is an organic one such as paint, which generally consists of resins, pigments and fillers, additives, and solvents. Topcoats or paints mainly rely on secondary bonding to metal surface, i.e., polar interactions such as hydrogen bonds and van der Waals forces, which are insufficient in adhesion for resistance to chemical attack, stress and weathering.

Steel producers use various organic and inorganic coatings to protect cold-rolled steel (CRS) sheets from corrosion during shipment and storage. The common practice of providing temporary corrosion protection for steel sheet is to apply a conversion coating. Traditionally, conversion coatings are produced by exposing CRS sheet or galvanized CRS sheets to phosphoric acid (phosphating process) or chromic acid (chromating process) or both. The latter provides more effective corrosion protection. However, serious environmental and health concerns have generated a great deal of interest in developing chrome-free conversion coatings. Most new developments are based on organic coatings.

It is well known to provide corrosion protection to steel sheets by coating with a liquid resin containing an organosilane coupling agent. U.S. Patent No. 5,077,354 (Woo and Marcinko, 1991) discloses an *in-situ* formed polymeric mixture comprising an acrylic graft copolymer of silicone resin used as a polymeric binder in powder paints. Silicone resin and ethylenic monomers are dissolved in a solvent heated to 50-150 °C, and mixed until polymerization is completed. A disadvantage of using this powder paint is believed to be that a good bond is not formed between the paint and steel substrate, because the silicone resin has already reacted when combined *in-situ* with the ethylenic monomers and will not act as a coupling agent between the acrylic layer and the substrate. In U.S. Patent No. 5,455,080, No.5,498,481 and No.5,539,031, van ooij (1995, 1996a and b) disclose a method of coating CRS or galvanized steel with a blended powder mixture including a thermosetting resin and a solid, non-hydrolyzed organosilane coupling agent. This mixture contains 0.01-10 wt.% organosilane having a melting temperature not greater than the curing temperature of the resin. It is believed that organosilane can diffuse to metal surface

and form a crosslinked layer during the curing step. U.S. Patent No.5,389,405 (Purnell, et al., 1995) and No.5,412,011 (Morris, et al., 1995) disclose non-chromium conversion coatings for metal surface such as aluminum, steel, and galvanized steel, consisting of an aqueous solution of an anionic polyacrylamide copolymer, an inorganic silicate, and an organofunctional silane.

There have been a few attempts to add reactive surfactants into polymer or other coating compositions for enhanced corrosion resistance. Sankaranaryanan and Subbaiyan (1993) found that adding 1 g/l octadecyl dithiocarbamate ($C_{18}H_{37}OCSSH$) to a phosphating bath could improve the corrosion resistance of phosphate treatment. van Alsten (1999) added alkyl bisphosphonic acids and zinc acetate (each in 1000 ppm) to a copolymer of ethylene and methacrylic acid. This mix is then melt-pressed into a film of ca. 2 mm in thickness on CRS panels. These panels are subsequently cured in a vacuum oven at 150 °C to allow the self-assembly process to proceed, and finally subjected to the delamination test in 0.1% NaCl solution. The SAM formation directly from competitive polymer melts appears more sluggish than from dilute solutions but property improvements of additive-containing polymers can be observed after several minutes of annealing time.

It is well known that organosulfur compounds have a strong affinity to metal substrate and can form a close packed SAM on metal substrate. There have been attempts to use this SAM to produce a corrosion-resistant coating [Jenning, 1996; Nozawa, 1997; Aramaki, 1999; Taneichi, 2001]. The present work is a new attempt to directly use sulfur-containing compounds to modify conventional resin solution for forming an endurable coating with enhanced corrosion resistance.

As discussed in the previous chapter, *l*-octadecanethiol (ODT) is capable of giving corrosion protection of 50 to 60 hours for EG steel as evaluated by SST. This coating, however, increases the water contact angle from 72° to 124°. Also, the surface energy decreases from 45.24 mJ/m² to 34.63 mJ/m², indicating the surface has become very hydrophobic. This hydrophobic surface may be useful for providing fingerprint free surface. However, it is very difficult to further coat the surface with resin and other topcoats.

The high hydrophobicity and the poor paintability of ODT coatings are due to the methyl terminals of ODT molecules. This problem may be resolved by modifying alkanethiol with a high-energy functionality such as hydroxyl (-OH), carboxyl (-COOH), amino (-NH₃), vinyl group (-CH=CH₂). Another technique is to construct a multiplayer with silane or other surfactants over the top of thiol coatings.

Initially, two kinds of thiols terminated with –OH and –COOH groups have been tested to explore the potential for improving the paintability and improving corrosion resistance simultaneously. This is a two-step process with hydroxyl thiol or carboxyl thiol as the first layer and the resin applying to the substrate in succession as the second layer. Subsequently, a one-step process has been developed with success by mixing the resin and thiol solution together and applying this mixture to the substrate. This mixture may be called as thiol-modified resin. This attempt has lead to a novel approach for this project.

4.2 EXPERIMENTAL

4.2.1 Reagents

The following reagents were ordered from Sigma-Aldrich Chemicals, Co. (i) *11*-mercapto-*1*-undecanol (MUO, HS(CH₂)₁₁OH); (ii) *16*-mercaptohexadecenoic acid (MCA, HS(CH₂)₁₅-COOH).

MUO can be dissolved completely in ethanol at concentration of 0.05 M. On the other hand, MCA could not fully dissolved in ethanol at the concentrations under test (0.025 M to 0.05 M). Its solubility seemed to be improved when the mixture of 4:1 ethanol/water was used as solvent to prepare a 0.02M solution. It was later found that MCA could dissolve very well in both ethanol and ethanol/water mix at slightly elevated temperatures. No attempt was made to dissolve these two reagents in water because of the limited quantity.

OTS (octadecyl triethoxyl silane) and OIC (octadecyl isocynate, C₁₈H₃₇NCO) were also purchased from Sigma-Aldrich Chemicals, Co. Resin and ODT are the same as used in previous tests. *I*-Butanol of HPLC grade was purchased from Fisher Scientific. Ethanol of 200 proof was manufactured by AAPER Alcohol & Chemicals Co.

4.2.2 Steel Samples And Coating Method

The EG steel plates were received from POSCO every a few months. They were stored inside a vacuum desiccator. It should be noted, however, that the samples are no longer free of oxidation after being stored for months in absence of an inert gas atmosphere.

For the two-step process, the sample was dipped in thiol solution for desired time and dried by blowing nitrogen stream or dried naturally in air. The sample was then put into an oven at

temperature of 120 °C for heating 5 minutes. As a second layer, the resin was applied with a #5 bar coater and also cured for 5 minutes at temperature of 150 °C.

For the one-step process, a 0.1-*M* ODT solution was prepared with ethanol unless specified otherwise. The resin solution was prepared by mixing 99 parts of polymer solution and 1 part of inorganic hardener solution by weight, both of which are provided by POSCO. The ODT solution and resin solution were subsequently mixed together in a desired ratio. The resultant mixture solution was applied to a test EG steel panel of 12×7.5 cm by using a #5 bar coater. The coated panel is then cured inside an oven with a temperature of 150 °C for 5 minutes. Alternatively, the coating may be cured at 300 °C for 14 seconds. As a result, a uniform, lightly gray-colored coating was formed on the steel panel with the expected thickness in the range of 1~2 μm.

4.2.3 Contact Angle and Surface Energy

A Rame-Hart goniometer was used to measure the contact angles. A small drop of liquid was placed by means of a hypodermic needle on the surface of a CRS plate. The contact angles were measured through the aqueous phase. The measurements were made at 3-6 different spots of a CRS plate, and the measured values were averaged.

Contact angle measurements were conducted with three different liquids, namely water, formamide, and 1-bromonaphthalene. The contact angle values were used to determine the surface free energy and its components of the CRS surface as introduced in Chapter 1.

4.2.4 Tafel Studies

A standard three-electrode electrochemical cell was used. The working electrode consisted of a CRS sheet coated with surfactant(s). The steel plate under test was connected to a potentiostat by means of a copper cable with the other side (coated) was in contact with the electrolyte in the cell. A platinum mesh was used as counter electrode, while a Luggin capillary connected to a standard calomel electrode (SCE) was used as reference electrode. The Luggin capillary was placed close to the working electrode to minimize potential drop.

The potential of the electrode was controlled by a potentiostat (Model 273A by EG&G), which in turn was controlled by a computer through GPIB interface. The Tafel studies were carried out using the 352 SoftCorr III Corrosion Measurement software from EG&G. The

potentials were scanned in the range of ± 250 mV from the open circuit potential (OCP) at a scan rate of 1~2 mV/sec.

The measurements were conducted in 5% NaCl solutions. The solution was aerated by compressed air during the test. The measurements were conducted at three parallel samples. The electrolyte solutions were replaced after testing 3 different treated samples. By fitting the data to the computer program, corrosion potential (E_{corr}) and corrosion current (i_{corr}) were determined. i_{corr} serves as a measurement of corrosion rate.

4.2.5 Salt Spray Test

SSTs were carried out in the manner as described in the previous chapters. The samples were taken out every 24 hours and returned to the chamber after pictures were taken as quickly as possible to maintain the continuity of salt fog exposure. SSTs were conducted for periods in the range of 120-264 hours. In the latter period of the project, POSCO's procedures of salt spray test were followed. The difference is that the samples are subjected to washing and drying before taking pictures.

4.2.6 Thickness Measurement

Ellipsometer is a widely used technique to measure the thickness of organic coating on metal substrate. In ellipsometry, when monochromatic incident polarized light impinges on a smooth reflecting surface, the reflected light is elliptically polarized. The polarization of the reflected light is then measured in terms of two parameters: Δ and Ψ . Δ is defined as the change in phase difference between the parallel component and the perpendicular component of the polarized light that occurs upon reflection; Ψ is the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients. The change in values of Δ and Ψ is a function of the thickness of the films on the reflecting surface, the refractive indices of the film and the surface [Tompkins, 1993].

This technique has a shortcoming. It requires a smooth and reflecting surface. However, both EG steel sample and phosphated EG steel studied in the present work are extremely rough. Therefore, the film thickness was measured with a weight-gain method in the project. The thickness reported in this thesis is actually an average value over the entire surface.

The thickness was calculated from weight gain of the plate after the coating was applied. The plate was weighed with an electronic balance of 0.1-mg resolution before and after the coating was applied and cured. The weight gain is usually in the range of tens of milligrams. Three samples were measured and the average value of the thickness was reported in this paper. The coated sample should not be weighed until it was cooled down to the room temperature. The following equation was used to convert the weight gain into the thickness:

$$\delta = \frac{10(W_c - W_0)}{\rho A} \quad [4.1]$$

Where, δ is the thickness of the coating (μm); W_0 and W_c are the weight of the plate before and after the coatings are applied (mg); ρ is the density of the dry resin film and it was determined to be 1.011 g/cm^3 for the resin used in this project; A is the coated area of the steel plate ($11 \times 7.5 \text{ cm}^2$ in the present work).

4.2.7 Fourier Transform Infrared Spectroscopy (FTIR)

For EG steel surface, RAIR spectra were collected on a BIO-RAD FTS 3000MX spectrometer equipped with a PIKE 80Spec reflectance attachment set at an angle of incidence of 80° . Dry air was used for purging. The spectra were acquired at 4 cm^{-1} resolutions and were averaged over 16 scans. Each spectrum was obtained by subtracting a background spectrum of a gold-coated mirror provided by PIKE. In order to collect IR spectra of powder sample of ODT, a pellet of about 2 mm thick was made from 20 mg ODT and 200 mg KBr mixture by using a Specadie P/N 3550 (Graseby Specac). The IR beam went through this pellet and the spectra were collected at 4 cm^{-1} resolutions and were averaged over 16 scans.

4.2.8 X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed at The Chemistry Department of Virginia Tech using a Perkin-Elmer model 5400 photoelectron spectrometer. The XPS works on the photoelectric effect. A Mg X -ray is directed to the surface of a solid and electrons are kicked off. The kinetic energy of electrons from certain element is measured with a hemispherical analyzer and Apollo Dn 3500 computer, and can be used to identify the elements from which electrons were emitted. The area

scanned was approximately 1×3 mm. The maximum etch depth was 20 nm. Quantification was based on peak area determined with a Shirley background with sensitivity factors determined by the instrument manufacturer.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Salt Spray Test

4.3.1.1 Two-Step Process: MCA Plus Resin Coating On EG Steel

Figure 4.1 shows the photographs of the samples of various treatments after 144 hours of salt spray test. These treatments included the control sample (EG steel), the reference sample (EG steel coated with pure resin), and the two-step coatings of MCA and resin under two dipping times in MCA solution: 5 minutes and 10 seconds. MCA was dissolved in ethanol at concentration of 0.025 M . After being taken out from MCA solution, the sample was rinsed with ethanol and then dried with nitrogen gas and heated at 120°C for 5 minutes. As the second step, they were then coated with resin by using a #5 bar coater, and finally cured at 150°C for another 5 minutes.

After 24 hours, EG steel (control) was seriously corroded with white rust covering the entire surface. Meanwhile, the resin-coated EG steel started to lose its original luster. At 48 hours, red rust appeared on the surface of EG steel sample, while white rusts became visible on the resin-coated EG sample. In contrast, the samples coated with MCA and resin by a two-step treatment remained undamaged after 120 hours. After 192 hours, white rusts appeared only in spots.

It is interesting to note that dipping time does not significantly affect the anti-corrosion performance of the bilayer coating of MCA and resin. As discussed in Chapter 3, a 10-seconds dip is believed as a sufficiently short time for the plant operation in steel mill.

In the present work, MUO was also tested. However, the results were not as good as MCA. This can be explained by the fact that it only possesses a shorter carbon chain, similar to the case reported in Chapter 3 where *l*-dodecanethiol (C12) was not able to produce an anti-corrosion coating on EG steel as good as *l*-octadecanethiol (C18) was. It is well accepted that only the thiols with appropriate alkyl chain length are capable of forming a compact, well-ordered film on metal substrates [Ulman, 1997 and 1998].

As reviewed in Chapter 3, other researchers studied the multilayer of MUO and silane on metal substrates [Aramaki, 1999; Nozawa, 1997, 1999; Taneichi, 2001]. It is commonly believed

that the thiols containing hydroxyl group can be modified with silanes to produce an ultra thin (~5 nm), closely packed, tightly networked, strongly chemisorbed, and highly water repellent film. This film can provide an excellent corrosion protection. In the present work, EG samples were coated with MUO and MCA, and subsequently immersed in BTSE, or OTS or OIC

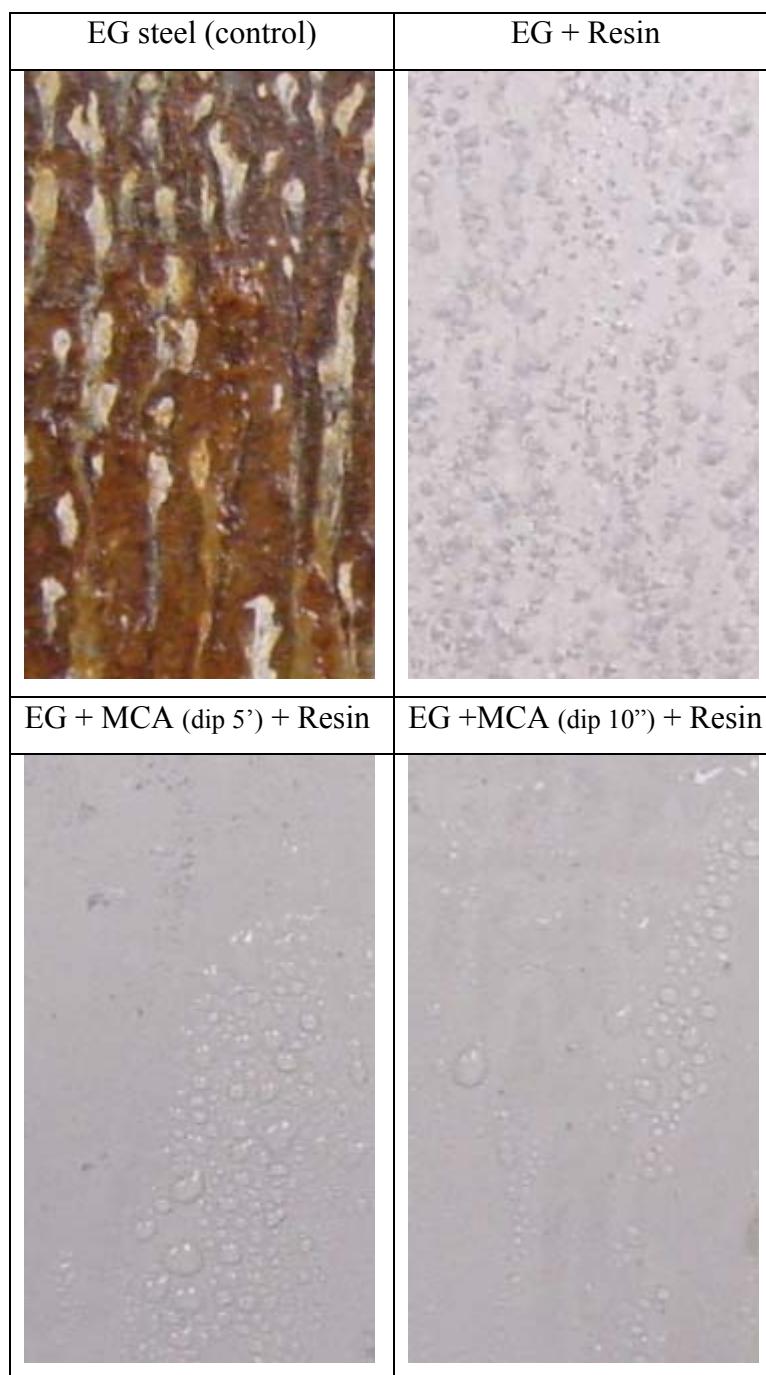


Figure 4.1 SST photographs of MCA plus resin coatings on EG steel (144 hours)

solutions. However, The SSTs did not show good results. One of the explanations may be that the sophisticated chemistry of this two-step coating was not exactly followed in the present work. It is also noted that these researchers evaluated the film mainly by electrochemical data or contact angle instead of an accelerated corrosion test.

In summary, MCA plus resin coatings can give a corrosion resistance over 120 hours. The dipping time can be as short as 10 seconds. On contrary, MUO does not give as good results as MCA.

4.3.1.2 Two-Step Process: Resin plus ODT Rinsing On EG Steel

ODT coatings can also be applied to painted surface. Figure 4.2 shows the comparison between three treatments after 240 hours of salt spray test. Sample 1 is the control sample of EG steel panel without any treatment. Sample 2 is the EG steel panel only coated with resin. The resin solution was applied to the steel panel with a #5 bar coater. A resin film of 1-2 μm thick is expected to form after being cured at 150 °C for 5 minutes. Sample 3 was treated in two steps. The first step involved the resin coating as applied in sample 2. The resin-coated panel was subsequently immersed in a 0.05 M ODT solution in ethanol for 5 minutes and finally dried in air at room temperature.

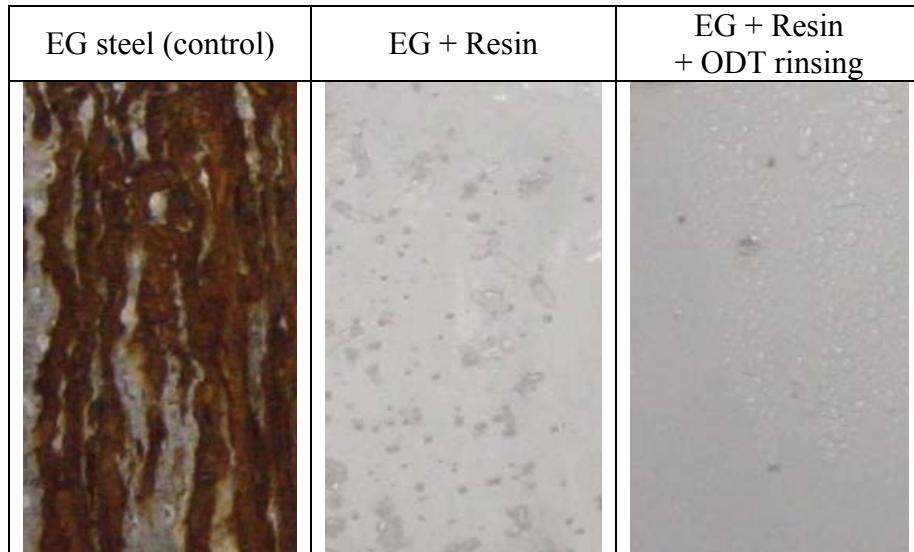


Figure 4.2 SST photographs of resin coatings plus ODT rinsing on EG steel (240 hours)

Salt spray test was conducted for these samples until 240 hours had passed. The test results shown in Figure 4.2 indicate that ODT rinsing can significantly improve the corrosion resistance when compared with resin coating alone.

Water contact angle measurement as shown in Table 4.2 demonstrates that ODT rinsing considerably increases the hydrophobicity of resin coatings, and therefore improves the corrosion resistance.

4.3.1.3 One-Step Process: Resin-Thiol Mix Coated On EG Steel

The objective of this test is to explore the possibility of using the mixture of a commercially available resin and various thiols. If the mixture is able to produce a robust, thin (ca.1~2 micron) film on metal surface that possesses a satisfactory corrosion resistance, the problem of paint wettability over ODT coatings will be solved. Furthermore, it will be possible to reduce the two-step process to a single-step process. Another feature of the one-step process is the simplicity because it has been a mature technology to apply resin onto steel sheets continuously with roller method in POSCO.

Figure 4.3 displays SST photographs of the following treatments after 144 hours of test:

- (i) EG steel (control);
- (ii) EG steel + Resin (reference);
- (iii) EG steel + resin-MCA (0.005 M) mix;
- (iv) EG steel + resin-MCA (0.0125 M) mix;
- (v) EG steel + resin-ODT (0.01 M) mix;
- (vi) EG steel + resin-ODT (0.025 M) mix.

A 0.025-M MCA solution and a 0.05-M ODT solution were prepared separately with ethanol. They were then mixed with resin solution in the arbitrary ratios of 1:4 and 1:1 by volume. Different thiol concentrations in the mixture were obtained as indicated above. The resin was actually diluted after the addition of thiol solutions. The modified resin was applied onto EG steel with a #5 bar coater. The coating was immediately cured at temperature of $150\text{ }^{\circ}\text{C}$ for 5 minutes. This treatment was expected to produce a film with the thickness of approximately 1~2 μm .

As introduced in the preceding section, the control sample corroded seriously after 24 hours of SST, while the reference sample coated with pure resin began rusting after 48~72 hours.

For the samples coated with resin-thiol mix that contains relatively higher concentration of thiol ($0.025\text{-}M$ ODT or $0.0125\text{-}M$ MCA in the mix), no white rust appeared even after 120~144 hours of SST. They exhibited a satisfactory corrosion resistance. In the case of lower thiol concentrations ($0.01\text{-}M$ ODT or $0.005\text{-}M$ MCA), however, the samples started corroding after 96 hours, but only a few isolated rust spots appeared on the surface at this time. It was concluded that the content of thiol in the mix has a pronounced effect on corrosion resistance. Even better results may be expected with increasing thiol concentration and fresher EG samples used as well.

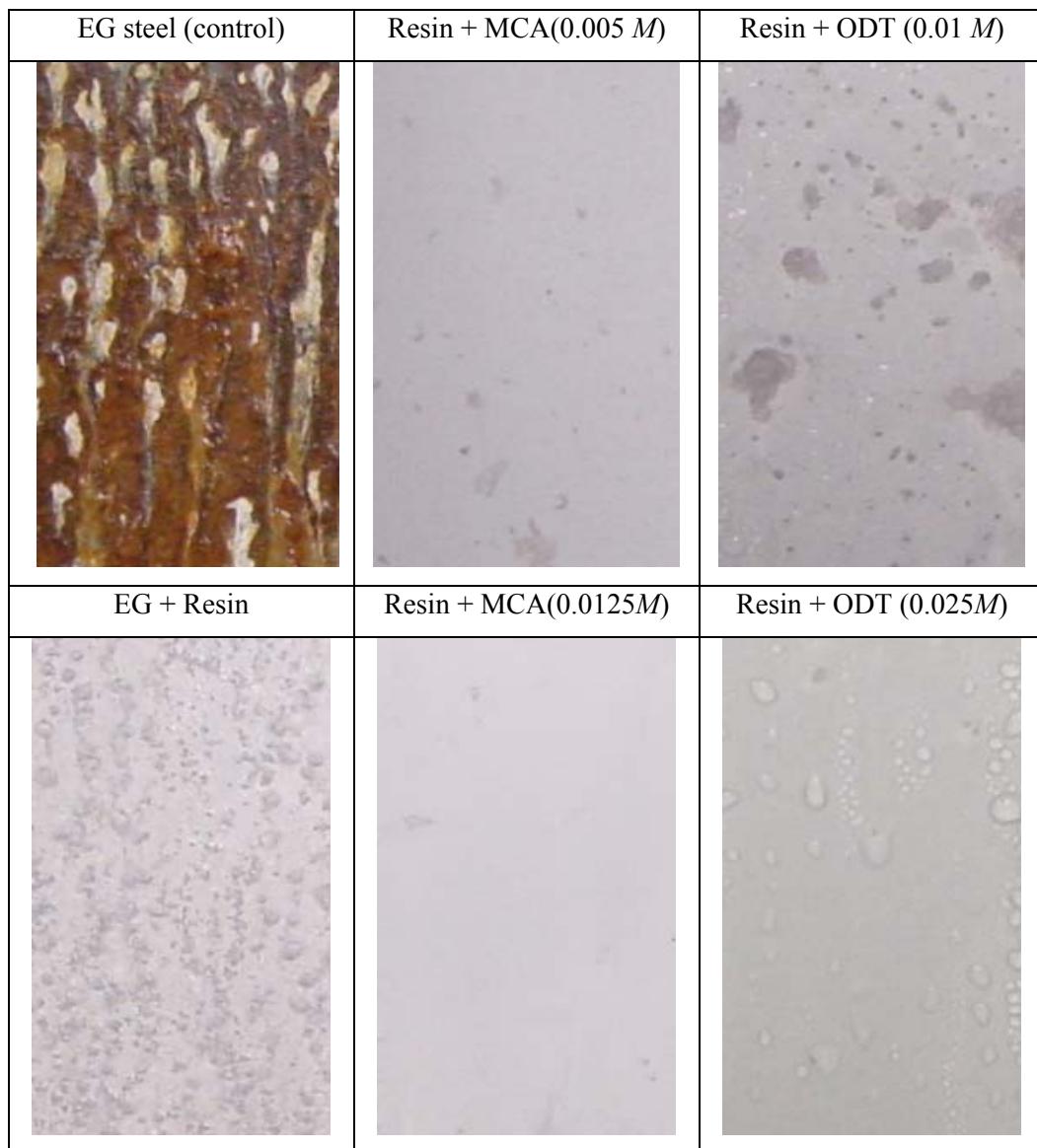


Figure 4.3 SST photographs of Resin-MCA mix and Resin-ODT mix coated on EG steel (144 hours)

4.3.1.4 Optimization Of Resin-ODT Mix Coatings On EG Steel

(1) Preparation of Samples

EG samples for this batch of test arrived at Virginia Tech on October 28, 2002 and were coated with resin-ODT mix on November 7, 2002. The salt spray test was conducted from November 11 to 22, 2002.

Resin solution was prepared in the same way as stated before. The base resin solution and the hardener solution were mixed in the ratio of 99:1 by weight. ODT solution was prepared by dissolving it in ethanol at the concentration of 0.1 M. Resin solution and ODT solution were then well mixed at the varying ratio from 9:1 to 4:6 by volume. ODT concentration in the resultant resin-ODT mix ranged from 0.01 M to 0.06 M as a function of the mixing ratio.

Resin-ODT mix was applied onto EG plates with a #5 bar coater. A coating of approximately 1~2 μm thick was expected after being cured in an oven with temperature of 150 °C for 5 minutes.

(2) Salt Spray Test

An EG steel plate without any treatment was placed inside the salt spray chamber as a control sample. Another EG steel plate, coated with pure resin, was tested as a comparison with these samples coated with resin-ODT mixture. As a reference, another EG plate that rinsed with chromate and then coated with resin (EG+Cr+resin), which was provided by POSCO, was also examined.

Figure 4.4 showed the photographs of this salt spray test. Exactly as observed before, the EG plate started to corrode shortly after it was put into the chamber (2~4 hours). After 24 hours, almost the whole surface of EG plate was covered with white rusts, while intact appearance still remained on the surface of other treatments.

At the time after 48 hours of salt spray test, the corroded spots emerged on the surface of the sample coated with pure resin. The rusts became more visible on the sample coated with 9:1 resin-ODT after 72~96 hours. Meanwhile, red rusting appeared on the control sample.

As the test proceeded, white rust came to sight successively on the surface of certain treatments. Corrosion initiated on the edge of 4:6 resin-ODT coated sample after 144 hours. Then, the coatings of 8:2 resin-ODT mix and 5:5 resin-ODT mix began corrosion after 168 hours and after 216 hours, respectively. The chromate-rinsed sample started rusting after 240 hours. Only two samples, coated with 7:3 resin-ODT and 6:4 resin-ODT mix, still remained in a good

condition after 264 hours. A film consisting of tiny water droplets still remained on the surface of these two samples, indicating that the coated surfaces were still hydrophobic.

The time for the initiation of rust is summarized in Table 4.1. It is evident that the optimal mixing ratio of resin to ODT was between 7:3 and 6:4. Correspondingly, the ODT concentration in the mix should be controlled in the range from 0.03 M to 0.04 M if the original ODT solution is prepared at the concentration of 0.1 M . The resin-ODT mix is superior to the chromate-treated sample under the optimal compositions.

There are three other advantages for the coating composition consisting of resin-ODT mix. Resin alone hardly gave a uniform coating with a good appearance on EG steel plate. When resin was applied onto the EG steel, the color of the coatings turned brown or black instantly. The same phenomenon happened for the resin-ODT mixtures with low ratio of ODT solution (9:1 or 8:2 for resin to ODT). However, the coatings of resin-ODT mix were always in uniformly gray color as the mixing ratio of ODT solutions increased. The second advantage is that the resin-ODT mix can make the coating thinner because of the dilution effect of solvents contained in

Table 4.1 SST hours for initiation and development of white rust on resin-ODT mix coated EG steel surface

Sample and Treatment	Composition of resin-ODT mix		SST hours for initiation and development of white rust	Rank of corrosion resistance
	Resin, % v/v	ODT* in the mix (M)		
EG	--	--	2~4	9
EG+Resin	100	0	48~72	8
EG+Resin-ODT (9:1)	90	0.01	72~96	7
EG+Resin-ODT (8:2)	80	0.02	168~192	5
EG+Resin-ODT (7:3)	70	0.03	264~288	1
EG+Resin-ODT (6:4)	60	0.04	264~288	2
EG+Resin-ODT (5:5)	50	0.05	216~240	4
EG+Resin-ODT (4:6)	40	0.06	144~168	6
EG+Cr+Resin	--	--	240~264	3

* 0.1 M in ethanol

ODT solution. The solvents will vaporize ultimately during the curing process. Another advantage is the simplicity of the one-step process for applying this mix to the substrate.

According to POSCO's experience, the film thickness is assumed to be 1~2 μm if a #5 bar coater is used to apply the resin coatings. However, the composition of coating materials also affects the thickness. Actually, the resin-ODT mix can reduce the thickness because the solvent has diluted the resin solution. This will be further discussed in the section of thickness measurement. Although the resin-ODT mix made the coating thinner, it was still able to increase the corrosion resistance significantly. One advantage of thinner organic coatings is better electrical properties, which will in turn result in a good formability of the coated steel sheet.

Attempts were also made to prepare ODT solution at higher concentrations. Actually, ODT may be dissolved in ethanol at concentrations up to 0.65 M (approximately 20.5% in weight) at elevated temperature. The stability of ODT solution mainly depends on the type of solvents, the concentration, and the temperature. When ethanol was used as the solvent, the solution of 0.2 M concentration could remain stable in 2~3 days without precipitates, while the stability could extend to one week for the solution of 0.1 M . But the solution of higher concentration was not stable enough. They started to precipitate in a few hours at room temperature.

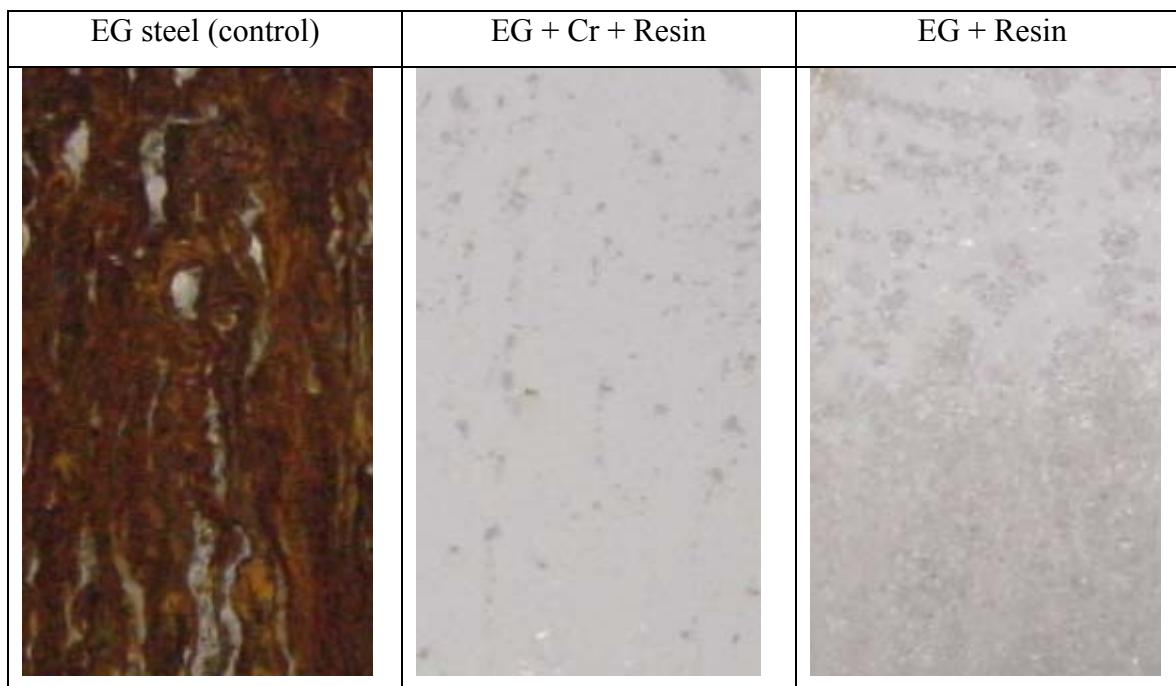


Figure 4.4 to be continued on the next page

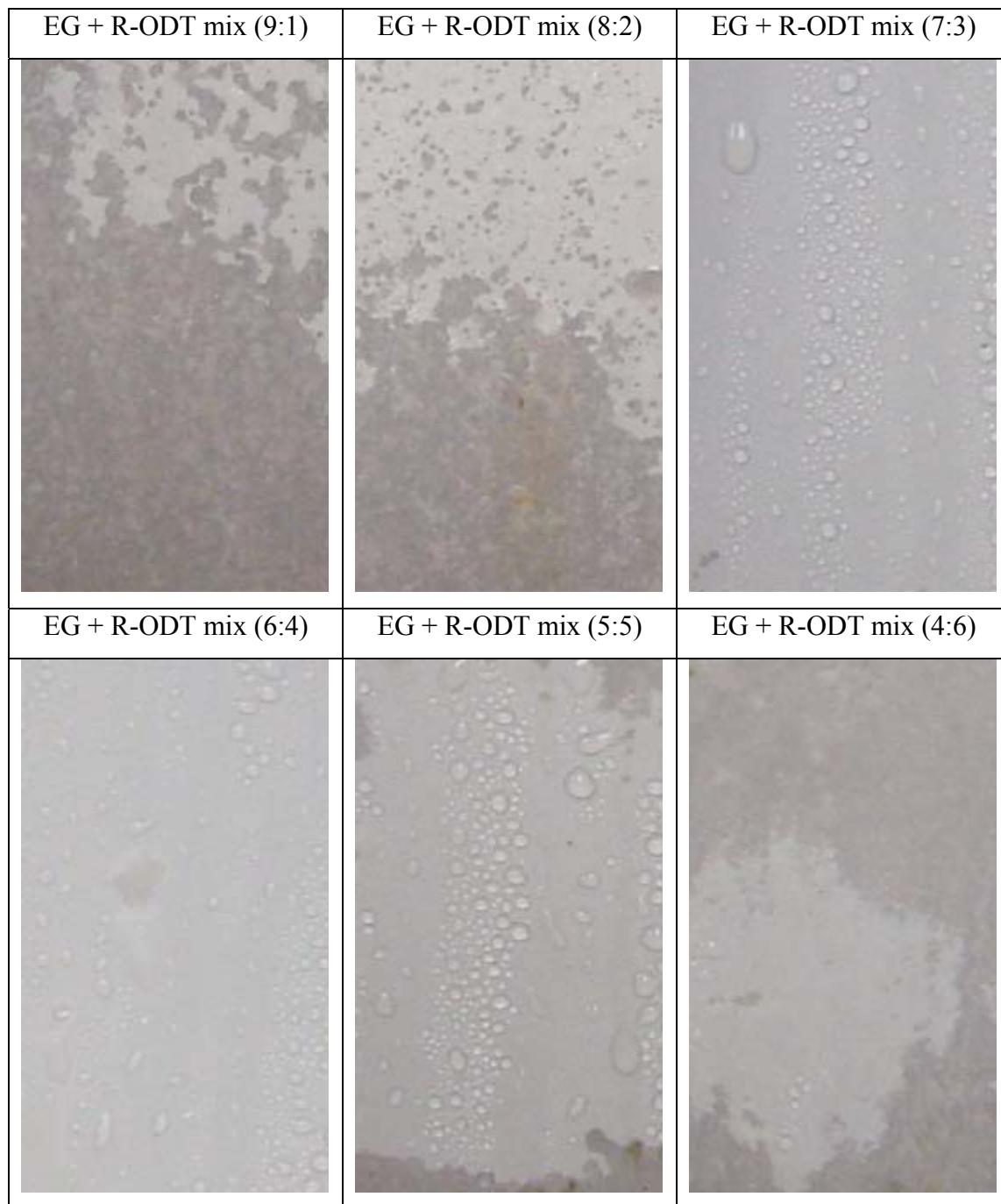


Figure 4.4 Photographs of salt spray test for resin-ODT mix coatings on EG steel (264 hours): the optimization test

4.3.1.5 Effect of Using Other Solvents for Resin-ODT Mix

Ethanol is a good solvent for ODT from the viewpoint of solubility and cost. But the high volatility is a disadvantage, which makes the ODT solution itself and the mix of resin and ODT solution unstable. POSCO has complained that as a shortcoming for industrial application.

In this test, *I*-butanol and *I*-octanol were used as an alternative of ethanol for dissolving ODT. Both of them dissolved ODT very well at concentration of 0.1 M, but the mix of resin and *I*-octanol-dissolved ODT could not produce a good-appearance coatings on EG steel. There were lots of white spots appearing on the coated surface after being cured at 150 °C for 5 minutes. Therefore, *I*-octanol was not a suitable solvent of ODT. When butanol was used to dissolve ODT, however, the resin-ODT mix can always produce a satisfactory film on EG steel surface. Furthermore, the ODT solution itself and the mix solution are very stable. There are no precipitate in the solution of the mixture even after 10 days.

Figure 4.5 shows the comparison between ethanol and *I*-butanol as the solvent of ODT. These pictures were taken after 168 hours of salt spray test. The concentration of ODT in both solvents was 0.1 M. The mixing ratio of resin and ODT solution for both treatments was arbitrarily determined as 7:3 by volume. The method of applying and curing the coating is the same as stated in the above section. As shown in Figure 4.5, when *I*-butanol was used a solvent,

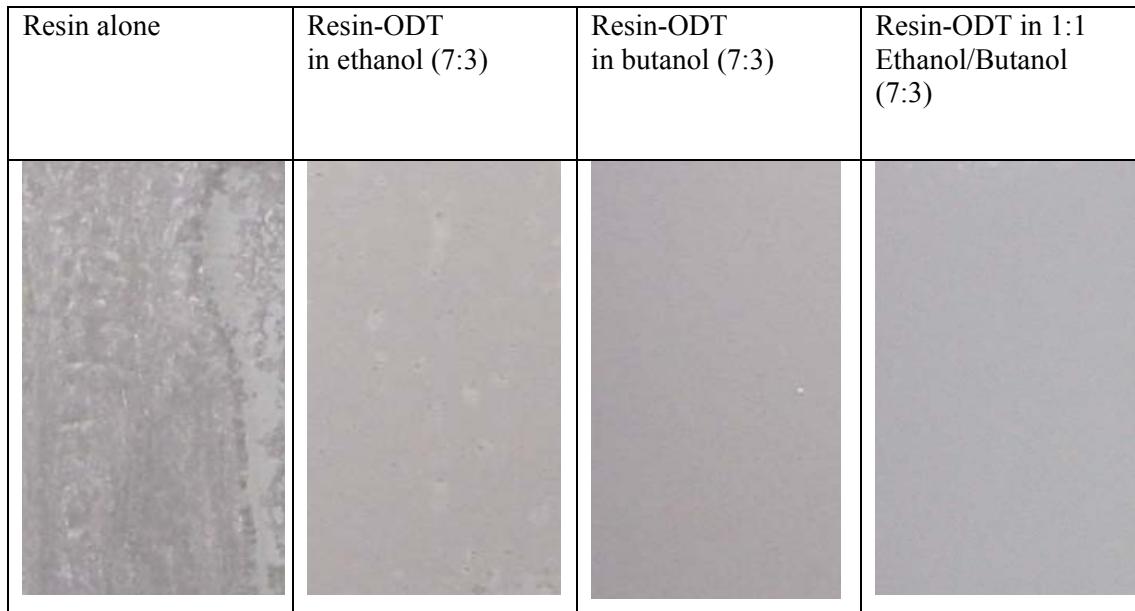


Figure 4.5 Photographs of salt spray test for resin-ODT mix coatings on EG steel with various solvents of ODT, (168 hours)

the resin-ODT mix coatings gave even higher corrosion resistance than that coatings when ethanol was used. The treatments with ethanol as the solvent did not perform as well as the previous tests. The reason may be the rigorous test conditions for this test, in which the test specimen were taken out, washed with tapwater and dried with nitrogen stream every 24 hours before pictures were taken.

However, the mixture of resin and ODT solution was somewhat viscous and showed unsatisfactory fluidity when *l*-butanol was used as the solvent of ODT. This problem was subsequently overcome with using the mixture of ethanol and butanol as the solvent. Figure 4.5 demonstrated that the resin-ODT coating was able to provide a very good corrosion resistance when the mixture of these two alcohols (1:1 by volume) was used as the solvent. Most importantly, the stability and fluidity of resin-ODT mixture were significantly improved. The properties can also be tuned by changing the ratio of butanol and ethanol.

4.3.2 Contact Angle And Surface Energy

4.3.2.1 Two-Step Process: Resin Coating plus ODT Rinsing On EG Steel

As discussed in Section 4.3.1.2, ODT rinsing could significantly improve the corrosion resistance of resin coatings. In order to understand the mechanism, water contact angle was measured on the surface of two treatments: resin coating alone, and resin coatings plus ODT rinsing. The resin was applied onto EG steel in the same manner as stated before. The ODT concentration was 0.05 M. The resin-coated EG plate was immersed in such an ODT solution for 5 minutes and dried naturally in air.

As shown in Table 4.2 and Figure 4.6, the contact angle increased from 90° to 128° due to the ODT rinsing, indicating that the ODT rinsing could substantially improve the hydrophobicity of

Table 4.2 Water contact angle at different phases of salt spray test over ODT-rinsed surface and resin-coated surface

Treatment	Before SST	After 120 hours of SST	After 240 hours of SST
Resin coating	90	66	54
Resin coating + ODT rinsing	128	120	77

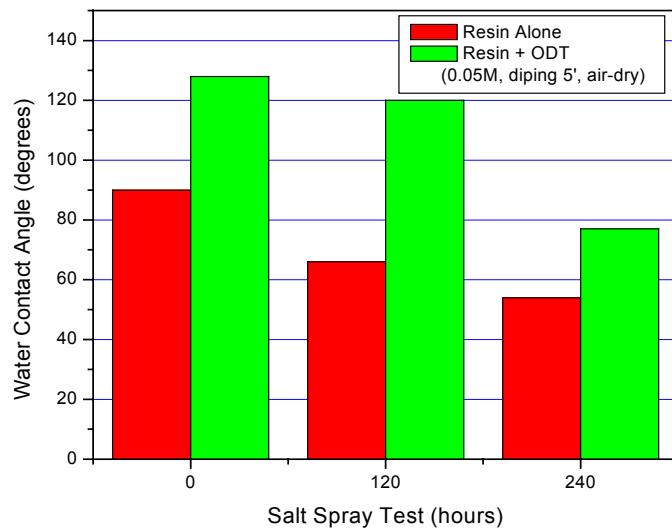


Figure 4.6 Change in water contact angle of resin treatment and resin plus ODT rinsing as salt spray test proceeds

resin-coated surface. As the salt spray test was proceeding, the water contact angle decreased for both treatments, indicating that the surface had become less hydrophobic. This can be attributed to the chemical attack of corrosive substances such as water, oxygen, and chloride ions during the salt spray. It was assumed that the ODT molecules mainly rely on the physical adsorption to attach onto the resin-coated surface.

The contact angle decreased at a much slower rate for ODT-rinsed surface ($0.067^{\circ}/\text{hour}$) than the resin-coated surface ($0.2^{\circ}/\text{hour}$) during the first 120 hours of salt spray test. It suggested that the ODT-rinsed surface was more corrosion resistant. At the end of salt spray test after 240 hours, the ODT-rinsed surface had a contact angle of 77° , still higher than 54° of the resin-coated surface. The former surface was almost free of rusting but lots of rusting spots appeared on the latter surface (see Figure 4.2). For the corroded surface, the contact angle was measured on the clean area instead of the rusting spots.

4.3.2.2 One-Step Process: Resin-ODT Mix Coated On EG Steel

EG surface coated with resin-ODT mix was characterized in term of surface free energy. As introduced in Chapter 1, three liquids with known surface tensions, namely 1-bromonaphthalene,

formamide, and water were used to measure the contact angle. From these contact angle data, surface free energy can be calculated with the Van Oss-Goods-Chandrey equation (Eq. 1.28).

Contact angle and surface free energy of resin-ODT coatings on EG steel are shown in Table

Table 4.3 Contact angle and surface free energy of resin-ODT coatings on EG steel

	Contact Angle (degrees)			Surface Free Energy (mJ/m ²)				
	water	BN	FA	γ_s	γ^{LW}	γ^{AB}	γ^+	γ^-
EG	72	4	51	45.25	44.29	0.96	0.02	9.82
EG+Resin	82	13	64	44.99	43.27	1.72	0.29	2.55
EG+Resin-ODT(9:1)	86	14	64	44.03	43.09	0.94	0.13	1.64
EG+Resin-ODT(8:2)	91	19	67	42.54	42.02	0.52	0.12	0.56
EG+Resin-ODT(7:3)	88	30	77	39.93	38.66	1.27	0.29	1.38
EG+Resin-ODT(6:4)	93	33	73	38.12	37.53	0.59	0.14	0.64
EG+Resin-ODT(5:5)	98	19	87	42.04	42.02	0.02	0.00	0.02
EG+Resin-ODT(4:6)	104	20	86	41.77	41.77	0.00	0.00	0.00
EG+Cr+Resin	87	20	67	42.90	41.77	1.13	0.26	1.22

FA-foramide; BN-bromonaphthalene

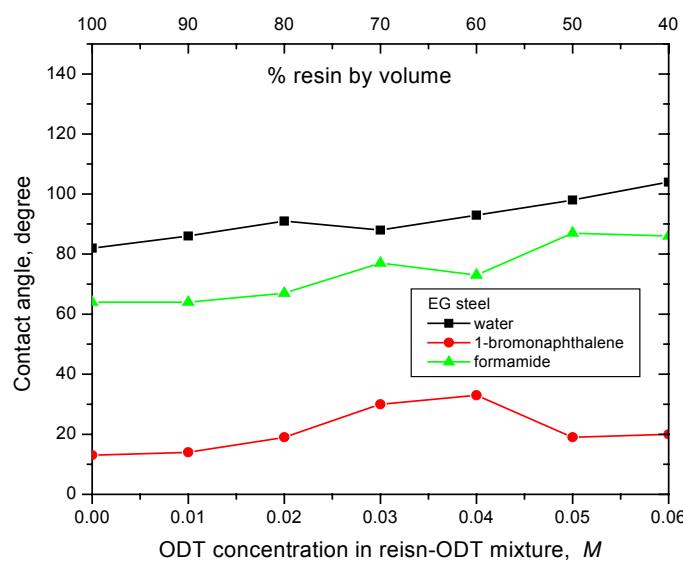


Figure 4.7 Contact angle of EG steel coated with resin-ODT mix under different mixing ratio

4.3, Figure 4.7 and Figure 4.8. The resin-ODT coating was applied onto the EG steel in the same manner as described in Section 4.3.1.4. The detailed information of resin-ODT mix was specified in Table 4.1.

Without any treatment, EG steel possessed the highest surface free energy ($\gamma_S = 45.25 \text{ mJ/m}^2$). Compared with those coated-samples, its basic component was also the highest ($\gamma^- = 9.82 \text{ mJ/m}^2$), although its nonpolar component was still the dominant component. Therefore, EG steel surface may be characterized as a weakly basic surface. After being coated with resin or resin-ODT mix, its total surface free energy decreased to some extent. For resin alone, its total free energy only decreased from 45.25 mJ/m^2 to 44.99 mJ/m^2 . Nevertheless, the ODT coatings could reduce surface free energy from 45.25 mJ/m^2 to 34.63 mJ/m^2 , as shown in Table 3.1. This difference can be attributed to the distinct composition of ODT and resin coating. As discussed earlier, ODT coating consisted of a SAM with its alkyl chains stretching outwards. This monolayer was closely packed, able to produce a highly hydrophobic surface. The resin, however, was known as a mixture mainly of modified acrylic polyethylene and aziridin. Thus, resin cannot give the same hydrophobic surface as ODT does because of its polar components.

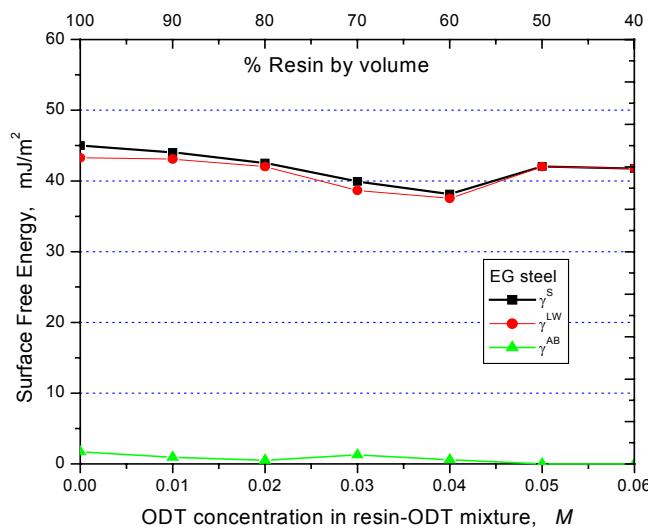


Figure 4.8 Surface free energy of resin-ODT mix coated EG steel under different mixing ratio

After ODT was added to resin solution, the surface free energies of resin-ODT coatings further decreased. This may be attributed to the orientation of ODT molecules in the resin-air interface. It was assumed that nonpolar groups of ODT molecules would concentrate on the top of coatings. At the mixing ratio of 7:3 and 6:4, the surface exhibits the lowest free energy with the values below 40 mJ/m^2 . However, the surface free energy increased slightly with more ODT added to resin as represented by higher mixing ratio of ODT to resin (5:5 or 6:4).

The relationship between the surface properties and the corrosion resistance will be discussed in detail in Section 4.3.8. Briefly, the low surface energy is helpful for improving the corrosion resistance of the organic coatings although it is not a decisive factor.

4.3.3 Tafel Studies

Table 4.4 and Figure 4.9 show the results of Tafel studies conducted on the EG plates coated with resin-ODT mix under different mixing ratio as specified in Table 4.1.

As shown in Figure 3.13, the corrosion current (i_{corr}) of bare EG steel was $49.04 \mu\text{A/cm}^2$, which was reduced to $8.78 \mu\text{A/cm}^2$ after being coated with ODT monolayers. In this test, its corrosion current was reduced to $4.21 \mu\text{A/cm}^2$ when EG steel was coated with pure resin. These data were fairly consistent with the results of salt spray test that revealed that the white rust appeared on the surface after 2~4 hours, 50~60 hours and about 72 hours for bare EG steel, ODT-coated EG steel and resin-coated EG steel, respectively.

Table 4.4 Corrosion current density of EG steel coated with resin-ODT mix under different mixing ratio

Treatment	Corrosion current density ($\mu\text{A/cm}^2$)	
	Before soaked in 1 M NaCl solution	After soaked in 1 M NaCl solution for 100 hours
EG+Resin	4.21	21.03
EG+Resin-ODT(9:1)	0.09	18.98
EG+Resin-ODT(8:2)	0.08	8.22
EG+Resin-ODT(7:3)	0.002	4.85
EG+Resin-ODT(6:4)	0.003	6.02
EG+Resin-ODT(5:5)	0.02	8.70
EG+Resin-ODT(4:6)	2.28	12.72

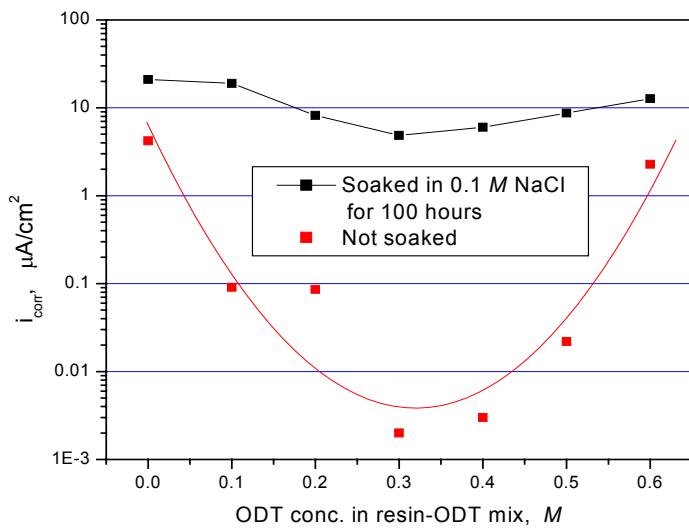


Figure 4.9 Corrosion current (i_{corr}) of resin-ODT mix coated EG steel under different mixing ratio

The corrosion current of bare EG steel increased to $21.03 \mu\text{A}/\text{cm}^2$ after it had been soaked in $1 M$ NaCl solution for 100 hours. This indicated that chloride ions and other corrosive substances had diffused to the metal/resin interface through the pores inside the resin matrix, and therefore accelerated the corrosion process.

The corrosion current reduced to “nA/cm²” scale when EG steel was coated with resin-ODT mix. It also depended on the mixing ratio of resin and ODT. The corrosion current was the lowest under the optimal mixing ratio of resin to ODT solution (7:3 and 6:4 by volume). Soaking the samples in NaCl solution increased the corrosion current. But the value of corrosion current under optimized coatings ratio (resin solution: $0.1 M$ ODT solution = 7:3 or 6:4) was still the lowest. The results of Tafel studies confirmed the optimization tests of salt spray as discussed in Section 4.3.1.4. The relationship between Tafel data and the corrosion resistance will be discussed in details in Section 4.3.8.

4.3.4 Thickness Measurement

It is well known that corrosion resistance of an organic coating depends on the composition, structure, and the thickness of the coating, which affect oxygen and water permeability. It also depends on the chemical bonds over the metal/coat interface. A robust organic film must have

less porosity and diffusion path to the external corrosive media. A thick organic coating tends to be more corrosion resistant. However, the need of corrosion resistance has to be compatible with the need for spot welding and electrical grounding. A thick coating is usually more electrically insulating, and it may deteriorate its grounding and weldability. To obtain a good grounding and weldability, the thickness of a conversion coating should be less than 1 to 2 μm . According to Kubato (2000), it still remains a challenge to achieve such a good corrosion protection by such a thin film without the use of chromate.

Figure 4.10 shows the thickness of resin-ODT coatings as a function of the mixing ratio of resin and ODT solution. The thickness was measured by weighing the plate before and after the coating was applied. The sample was prepared in the same manner as introduced in Section 4.3.1.4. The film became apparently thinner as more ODT solution was added. For pure resin, the film thickness was about 2.5 μm but the thickness reduced to 1.8 μm when ODT solution was added in the resin:ODT ratio of 7:3 or 6:4. The decreased thickness of resin-ODT mix coatings was resulted from the dilution effect of solvent. When ODT solution (0.1 M in ethanol) was added to resin solution, it brought in a quantity of solvents (ethanol). The solvent would finally vaporize during the curing process of the coatings. Previously, it was assumed that the film thickness was predominately controlled by the size of the bar coater. Now it is realized that the

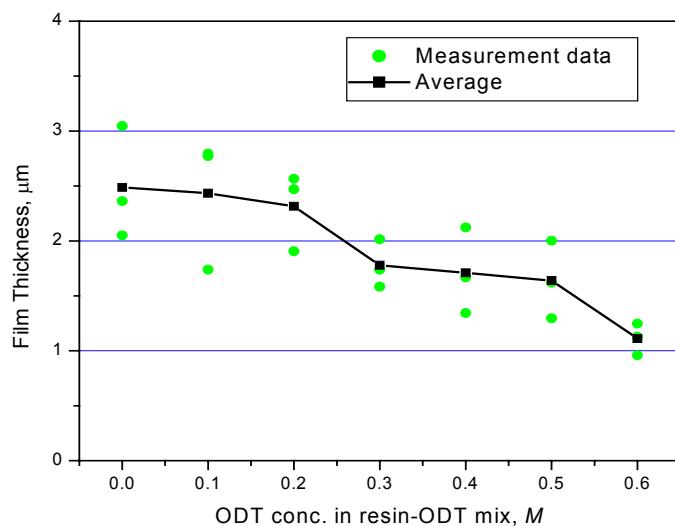


Figure 4.10 Film thickness of resin-ODT coatings on EG steel as a function of mixing ratio

composition of coating materials also affects the film thickness to great extent.

Obviously, the dilution effect of solvent has a positive impact to control the thickness. As discussed above, the resin-ODT coatings at the optimal mixing ratios could provide greater corrosion resistance even though the film is thinner than that produced by pure resin. The resin-ODT mix may produce a satisfactory coating that possesses high corrosion resistance and acceptable electrical property.

4.3.5 Surface Characterization: XPS Analysis

Figure 4.11 gives two of the *X*-ray photoelectron spectra obtained from the resin-coated EG steel surface and resin-ODT mix (7:3) coated EG steel surface. The atomic concentrations of these coatings are shown in Table 4.5.

The most intense peak is located at 285 eV for both treatments. This binding energy can be assigned to C1s. Carbon is the dominant element contained in the resin coating and resin-ODT coating. Its concentration reaches over 90%, and does not change very much for different mixing ratios of resin to ODT and in different etch depth from 0 to 20 nm.

The binding energy around 163.7 eV may be assigned to S2p. Sulfur could only be detected in the coatings of resin-ODT mix. There is no sulfur in pure resin coatings. The highest concentration of sulfur (3.09%) is observed on the topmost surface under the mixing ratio of 5:5. Interestingly, the sulfur is unequally distributed over the depth of the coatings. It also depends on the mixing ratio of resin and ODT solution. Generally, more ODT addition may result in higher sulfur content in the coatings. In terms of sulfur concentration in the coating, there is an optimal mixing ratio of resin to ODT solution. The sulfur content reaches the highest values when the resin and ODT solution are mixed in the ratio of 7:3, or 6:4 or 5:5. The sulfur concentration of the coatings is well correlated with the results of salt spray test. As shown in Table 4.1, the EG steel coated with resin-ODT mix under these three mixing ratios had given the highest corrosion resistance. This correlation will be further discussed in Section 4.3.8.

Sulfur concentration decreases as the surface is etched deep. The sulfur should concentrate over the deep layer if it reacted with zinc. This phenomenon may be attributed to the rough surface of the EG steel. It must be noticed that a 20 nm etch was not deep enough for a coating of 1~2 μm . This XPS instrument cannot etch deeper, and thus does not present a whole pictures of sulfur distribution over the section of the coating.

O1s peak is detected at the peak near 532.8 eV. Obviously, the oxygen is brought in by the carbonyl groups of the acrylic type resin. The concentration of oxygen is around 5% for all treatments.

Si2p peak appears at the binding energy 103.9 eV. Therefore, It is postulated that the original resin solution contains the silicon, most likely in the form of silicate or silane. According to the element distribution as shown in Table 4.5, the concentration of silicon increases when the surface is etched deeper. There is almost no silicon detectable on the top surface of 0~10 nm. The concentration of silicon increases to about 3% when the surface was etched to the depth of 20 nm. The silicon-containing molecules in the resin may have formed a strong bonding to zinc substrate. Therefore, more silicon has been detected over the deeper layer of the coatings.

There is a weak peak around the binding energy 1022.8 eV, which may be assigned to Zn2p3. This indicates that a small amount of zinc is detected on the surface. As shown in Table 4.5, the zinc concentration is very low (0~0.3%). There is no zinc detectable in most cases, even after the specimen has been etched for 20 nm. Compared with the high concentration of zinc in the case of ODT monolayer coating as shown in Table 3.5, one may conclude that the relatively thick coating of resin or resin-ODT mix has flattened the rough surface of EG steel to some extent. The rarely detectable zinc and the extremely low concentration indicate that there are still some zinc tips exposed outside. This zinc may become the most vulnerable spots for corrosion attack. This can help explain the reason that the rusting is always initiated from some points and extends over the surface during the salt spray test.

Table 4.5 Elemental composition of resin-ODT mix coatings on EG steel

Coating system on EG steel	Atomic Concentration, %														
	before etch					after 10 nm etch					after 20 nm etch				
	C	O	S	Zn	Si	C	O	S	Zn	Si	C	O	S	Zn	Si
Resin	95.17	4.64	0.00	0.19	0.00	90.48	5.89	0.00	0.25	3.38	91.22	5.28	0.00	0.20	3.30
Resin-ODT, 9:1	93.52	5.58	0.10	0.00	0.80	89.22	7.31	0.00	0.00	3.46	87.80	8.32	0.00	0.00	3.89
Resin-ODT, 8:2	94.79	4.53	0.28	0.00	0.40	93.32	4.55	0.00	0.00	2.13	91.41	5.80	0.01	0.00	2.78
Resin-ODT, 7:3	94.19	4.16	1.16	0.31	0.19	90.37	5.91	0.17	0.08	3.47	91.72	4.94	0.27	0.00	3.08
Resin-ODT, 6:4	95.24	2.32	2.10	0.00	0.34	97.90	0.70	1.40	0.00	0.00	98.20	0.94	0.87	0.00	0.00
Resin-ODT, 5:5	94.09	2.11	3.09	0.00	0.71	94.61	2.96	0.92	0.00	1.52	94.01	3.32	0.79	0.00	1.88
Resin-ODT, 4:6	94.01	4.81	0.47	0.00	0.71	93.81	3.89	0.27	0.00	2.03	92.65	4.50	0.18	0.00	2.67

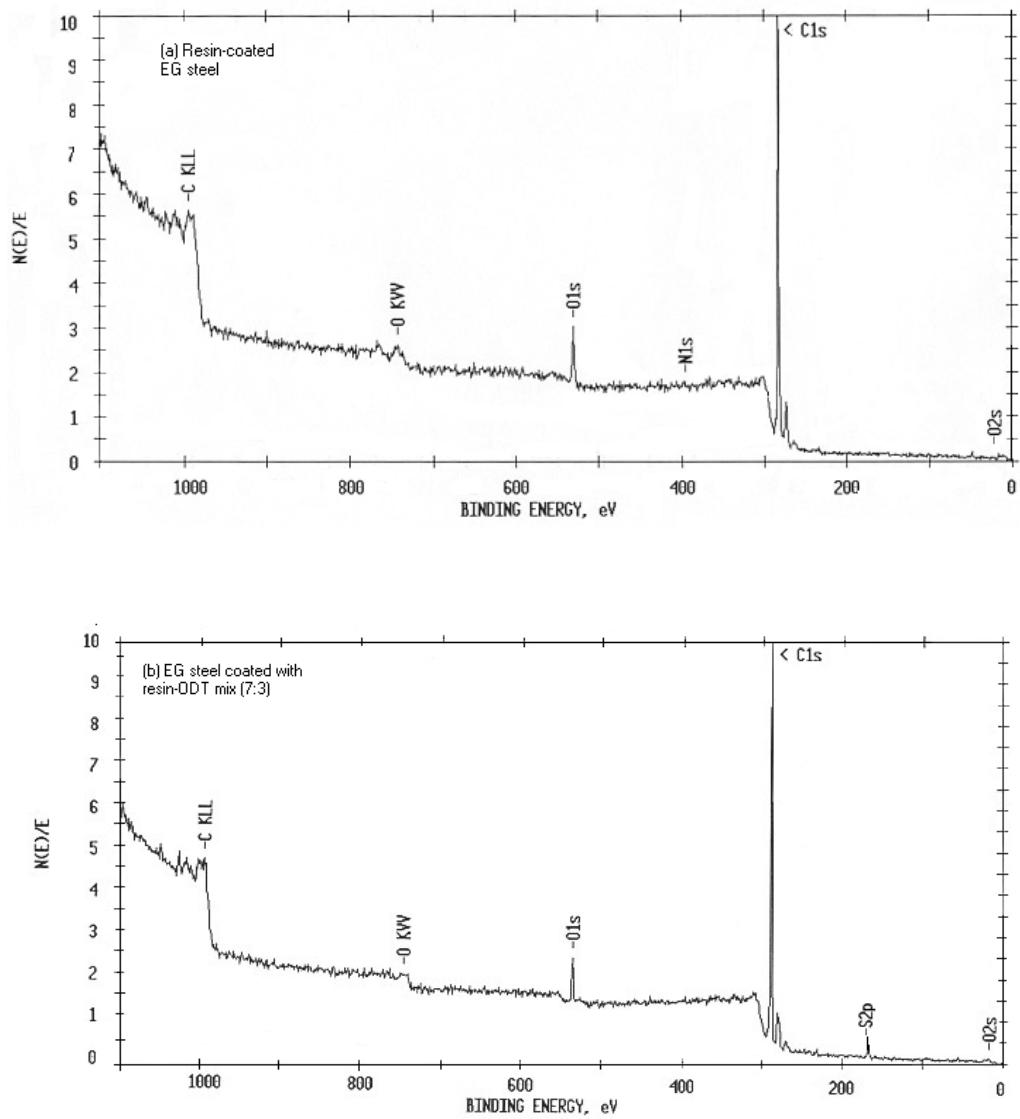


Figure 4.11 XPS spectra of EG steel coated with resin (a) and with resin-ODT mix (7:3) (b), without etch for both.

4.3.6 Surface Characterization: FTIR Studies

Figure 4.12 displays a group of RAIR spectra of EG steels coated with resin alone or resin-ODT mix under various mixing ratios. The bands at approximately 2931~2950 cm⁻¹ and

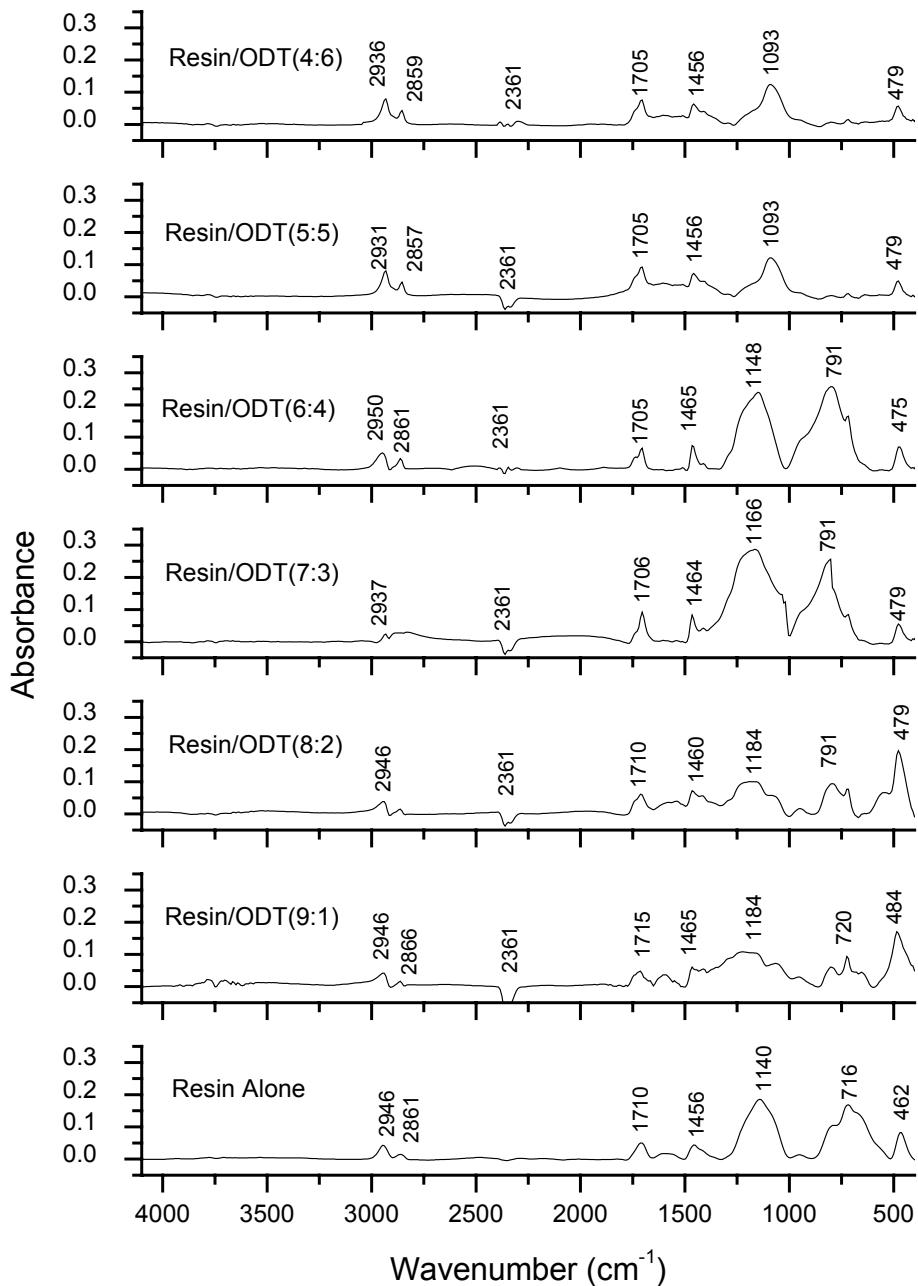


Figure 4.12 IR spectra of ODT-coated EG steel surface at different mixing ratio of resin and ODT

$2857\text{--}2866\text{ cm}^{-1}$ are assigned to the CH_3 and CH_2 stretching mode. The bands at $1456\text{--}1465\text{ cm}^{-1}$ and $716\text{--}720\text{ cm}^{-1}$ should correspond to CH_2 bend and CH_2 rock mode, respectively. These alkyl groups should originate mainly from the hydrocarbon chains of acrylic resin.

The distinctive features of the FTIR spectra of resin or resin-ODT coatings include an ester carbonyl band at approximately $1705\text{--}1715\text{ cm}^{-1}$, a SiOC or SiOSi band at $1093\text{--}1166\text{ cm}^{-1}$. Obviously, the carbonyl groups exist in the acrylic resin while the silicon-containing molecules are used as the additives of the resin solution.

A peak at 2361 cm^{-1} can be seen in all spectra of resin-ODT coatings except for the pure resin coating. As discussed in Section 3.3.7, this band may be caused by the adsorption of carbon dioxide or the oxidation product--zinc carbonate on EG steel. Lack of this peak in pure resin coating may be explained by the fact that the pure resin coating is thicker so that it has covered the substrate more completely.

The absorbance bands at approximately $462\text{--}484\text{ cm}^{-1}$ in all spectra may be accounted for as a ZnO absorbance (Manov, 2000). There was still some zinc exposed outside in spite of the relatively thick coatings. The bands at 791 cm^{-1} may be assignable to the C-S group for the resin-ODT coatings under the mixing ratio of 6:4, 7:3 and 8:2. But this peak disappears under the resin:ODT ratios of 5:5 and 4:6. This is not completely consistent with the sulfur concentration obtained by XPS analysis, in which high sulfur content was also detected under the mixing ratio of 5:5. However, the appearance of C-S peaks can result in high corrosion resistance.

4.3.7 Surface Morphology: AFM

Images of EG steel coated with resin and resin-ODT mix were obtained with a NanoscopeTM 3100 AFM (Digital Instruments). Figure 3.13 and Figure 3.14 show the images and the section analysis of these two treatments. The ratio of resin to ODT solution (0.1 M) was 7:3 by volume for the sample under test. Lots of tiny islands could be observed on the surface of resin-coated EG steel. This is because the vertical detection resolution for the pure resin coating is only 30 nm so that more details have been probed. On the other hand, the vertical resolution for resin-ODT coatings is 150 nm. So, its surface image seems smoother.

The surface roughness may be estimated from the section analysis. The roughness of resin-coated surface is about 30 nm but it is 80 nm for the resin-ODT coated surface. The different roughness of two treatments may be attributed to the difference of the film thickness.

Apparently, a thick organic film may help flatten the rough surface. As discussed in Section 4.3.4, resin-ODT mix coating ($1.8\text{ }\mu\text{m}$) is thinner than the resin-coated surface ($2.5\text{ }\mu\text{m}$) because of the dilution effect of solvents. Therefore, the resin-ODT mix coating is rougher than the coating of pure resin.

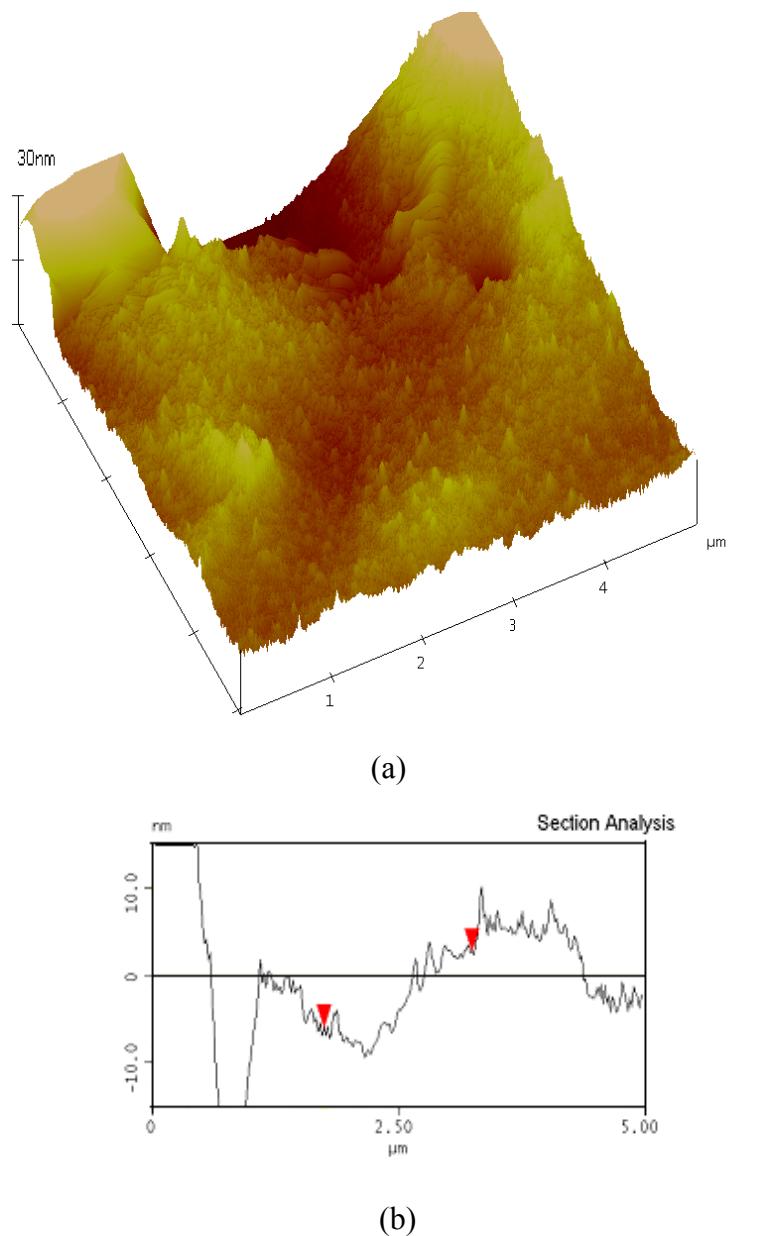
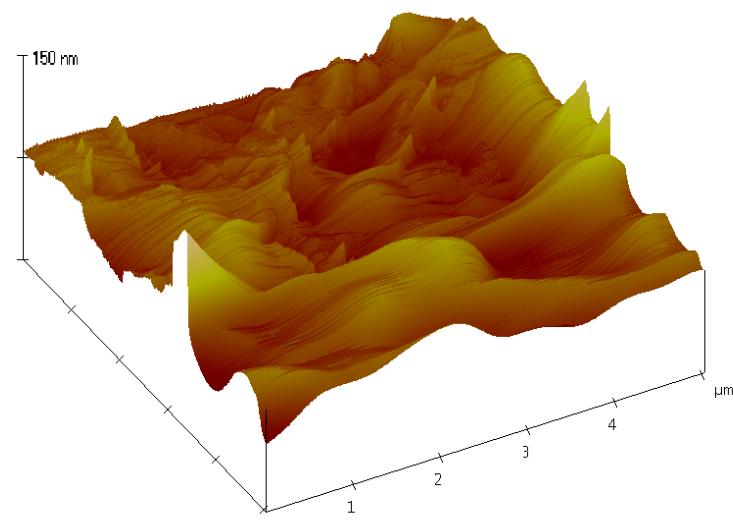
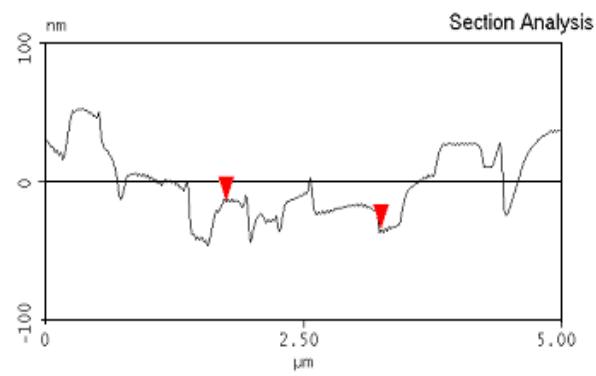


Figure 4.13 AFM image of resin-coated EG steel (a), and the section analysis (b)



(a)



(b)

Figure 4.14 AFM image of resin-ODT coating (7:3) on EG steel (a), and the section analysis (b)

4.3.8 Mechanism of Corrosion Resistance of Resin-ODT Mix Coatings

Figure 4.15 shows the correlation between the surface free energy and corrosion resistance. Corrosion resistance is represented by the time when white rusts starts to appear on the coated surface during salt spray test. In general, the coating with lower surface free energy can endure longer salt spray. Under the optimal mixing ratios of resin to ODT (7:3 and 6:4), the surface free energy reached the lowest value (below 40 mJ/m²), and the longest salt spray hours without rusting were achieved (over 264 hours). It suggests that the surface tension of coated surface has played a role in the improvement of corrosion resistance, although it is not a predominant factor among other parameters such as the bond strength between the substrate and the organic coating, and compactness of the coatings.

Low surface free energy must have been caused by the presence of ODT molecules. The surface free energy was the lowest when more ODT molecules had incorporated into the resin matrix under the optimal conditions. It is thought that the majorities of ODT molecules had orientated in the manner of their nonpolar methyl groups pointing outside, therefore the surface free energy was reduced. XPS analysis confirmed the high concentration of ODT molecules in the surface under the optimal conditions, since more sulfur had been detected over the surface.

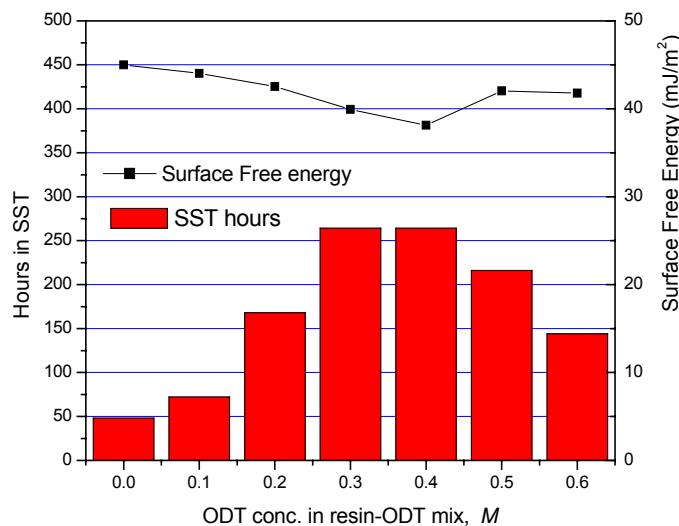


Figure 4.15 Correlation between surface free energy (γ_s) and corrosion resistance of resin-ODT mix coatings on EG steel

Figure 4.16 shows the relationship between corrosion current (i_{corr}) and the corrosion resistance. Corrosion current is generally thought to represent the corrosion rate of a material. Low corrosion current corresponds to high corrosion resistance and slow corrosion rate. The value of i_{corr} was obtained from Tafel studies on the EG steel coated with resin-ODT mix under various mixing ratios. The coated EG steel had been soaked in 1 M NaCl solution for 100 hours before tested. Corrosion resistance was evaluated by salt spray test. The resin-ODT coating gave

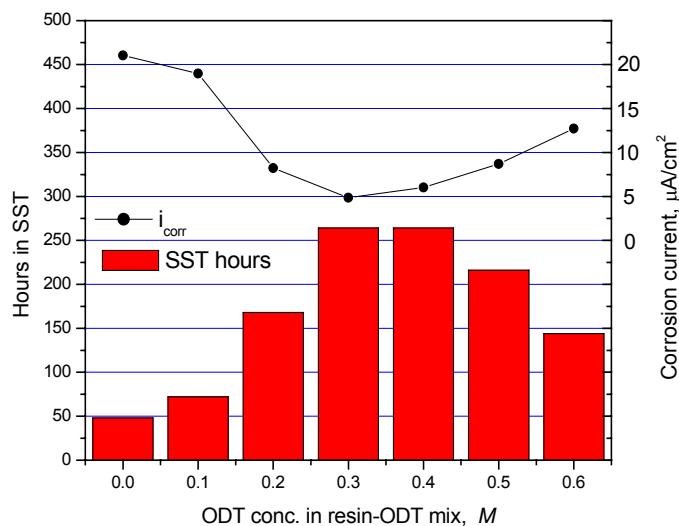


Figure 4.16 Correlation between corrosion current (i_{corr}) and corrosion resistance of resin-ODT mix coatings on EG steel. The coated samples had been soaked in 1 M NaCl solution for 100 hours.

the highest corrosion resistance and the lowest corrosion current under the optimal mixing ratio of resin to ODT solution (7:3 or 6:4). The decreased corrosion current of the optimized mixture after the coating was soaked in NaCl solution indicates that the coating is more resistant to the diffusion of corrosive substances such as water, oxygen and chloride ions. This may be explained by the assumption that the small ODT molecules must have filled the pores of resin matrix and thereby make the coating less porous, less permeable.

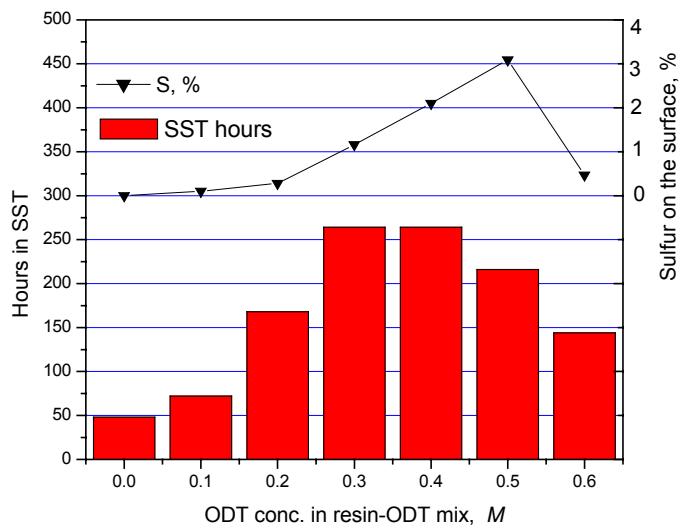


Figure 4.17 Correlation between sulfur concentration on the coated surface (S, %) and corrosion resistance of resin-ODT mix coatings on EG steel

Figure 4.17 shows the relationship between the sulfur concentration in the coated surface and corrosion resistance. The sulfur concentration was obtained with XPS analysis on the coated surface before etch. Obviously, the high sulfur content in the coatings can result in higher

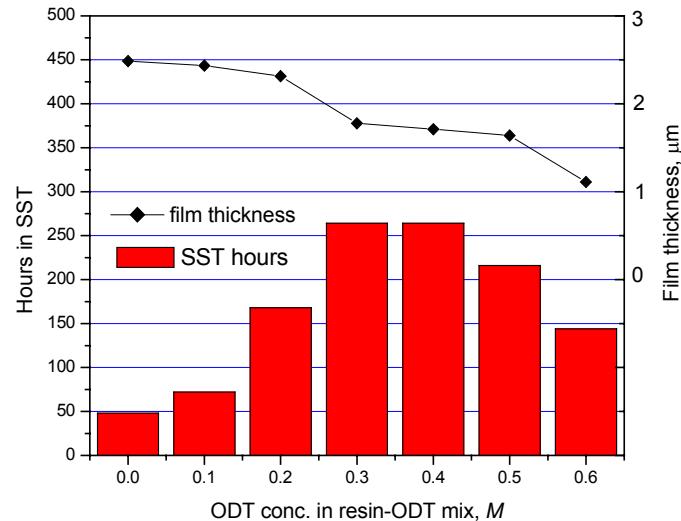


Figure 4.18 Relationship between film thickness (δ) and corrosion resistance of resin-ODT mix coatings on EG steel

corrosion resistance. Higher sulfur concentration represented more ODT molecules contained in the coating. These ODT molecules may make the coating more hydrophobic on the surface and less porous inside.

Figure 4.18 demonstrates the relationship between the film thickness and corrosion resistance of resin-ODT mix coating. There is no correlation between them. Thicker coating does not necessarily generate a higher corrosion resistance. Therefore, it may be concluded that the thickness of an organic film is not a critical parameter to promote the corrosion resistance as presumed before. The corrosion resistance of an organic coating mainly depends on the composition, structure and surface free energy of a coating.

In conclusion, the mechanism that ODT significantly improves the corrosion resistance of resin coatings may be ascribed to the following factors:

- (i) Establish a strong bond between zinc and thiol group (RS^-) by the chemical reaction as described in eq. [3.1]. This chemical bond is helpful for making a robust adhesion between resin and zinc surface due to its much higher bond energy than that of physisorption between convention polymer and metal substrate.
- (ii) Decrease the surface free energy of resin-coated surface due to the orientation of ODT molecules in the interface of resin and air, which help shield off the attack of moisture and other corrosive substances contained in the saltwater.
- (iii) Fill the pores inside resin coatings with ODT molecules, which makes the coating less porous, more compact, and more resistant to the chemical attack.

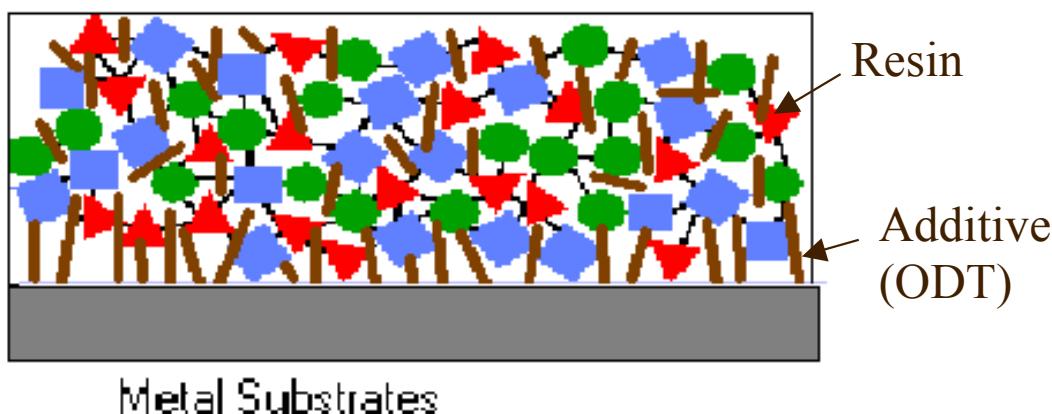


Figure 4.19 A schematic model of resin-ODT mix coatings on metal substrate to explain the mechanism of corrosion resistance improvement

Based on the discussions above, a model as shown in Figure 4.19 is proposed to explain the mechanism of resin-ODT mix coating for the improved corrosion resistance. It illustrates the enhanced bonds between the additives (ODT) and the substrate, the hydrocarbon chains of ODT on the top surface and the filling of the pores in resin matrix by the small additive molecules.

4.4 CONCLUSIONS

The salt spray tests were conducted on several coating systems to evaluate the corrosion resistance. The primary objective is to develop a practical coating composition for EG steel that may achieve 120 hours and over of corrosion resistance as evaluated with salt spray test.

The first group of reagents used in the present work was the thiols terminated with various functional groups such as carboxylic (-COOH) and hydroxyl group (-OH). They are supposed to make a relatively high-energy surface and therefore promote the adhesion of top resin coating. *11*-mercapto-*1*-undecanol (MUO) and *16*-mercaptohexadecenoic acid (MCA) were tested as the first layer of coating prior to the application of resin topcoats. MCA plus resin coating successfully withstood over 120 hours of salt spray test. MCA was dissolved in ethanol at the concentration of 0.025 *M*. As the first step, the EG steel was immersed in MCA solution for 5 minutes or 5 second, and then rinsed with ethanol, and dried with nitrogen gas and heated at 120 °C for 5 minutes. As the second step, MCA-coated EG steel was subsequently applied with resin by using a No. 5 bar coater, and finally cured at 150 °C for 5 minutes. It was found that 5-seconds dipping could give the same corrosion resistance as 5-minutes dipping. MUO did not work well because its short chain was not as effective.

Another two-step process was tested with resin applied as the first layer and then rinsed with ODT solution. The resin was applied and cured in a conventional manner, and then immersed in a 0.05 *M* ODT solution for 5 minutes, and finally dried in air. However, the resin could not readily be applied onto the EG steel. Its appearance was not satisfactory because of discoloration over EG steel surface. This coating system could also give over 120 hours of corrosion resistance. ODT rinsing could improve the corrosion resistance of resin-coated EG steel because it increased the surface hydrophobicity significantly. The contact angle increased from 90° to 128° due to the ODT rinsing. The contact angle decreased at a much slower rate for ODT-rinsed surface (0.067 °/hour) than the resin-coated surface (0.2 °/hour) during the first 120 hours of salt spray test. It suggested that the ODT-rinsed surface was more corrosion resistant. Another

shortcoming of this process was the extremely hydrophobic surface that is not compatible with further painting.

Subsequently, a one-step process was tested with mixing resin solution and thiol solution together. MCA and ODT were added to resin solution separately in a certain ratio. The mix was then applied to EG steel by using a No. 5 bar coater and cured at 150 °C for 5 minutes. This treatment was supposed to produce an organic film of 1~2 µm on EG steel. Both treatments were able to give over 120 hours of corrosion resistance. The higher the thiol concentration in resin-thiol mix, the greater the corrosion resistance.

The process of resin-ODT mix coating was then optimized with salt spray test. ODT was dissolved in ethanol at the concentration of 0.1 *M*. This solution was mixed with resin solution under various mixing ratios. These mixtures were applied to EG steel for corrosion test and characterization. EG steel coated with resin-ODT mix could resist over 200 hours of salt spray under optimal conditions (7:3 or 6:4 by volume for resin to ODT solution). The water contact angles of resin-ODT coated surface increased by 6~11° from 82° of pure resin coating, and thereby the surface free energy decreased to less than 40 mJ/m² from 45.25 mJ/m².

Other solvents were also tested for preparing ODT solution. *I*-Butanol as a solvent of ODT was better than ethanol in term of the solution stability and the corrosion resistance of the resultant coating.

Film thickness measurement indicated that resin-ODT mix decreased the film thickness because of the dilution effect of solvents. Pure resin coating produced a 2.5 µm film but the thickness decreased to 1.8 µm for resin-ODT mix coating. Thinner film would help improve the electrical property of the organic coating.

Tafel studies confirmed the optimization tests. The corrosion current or corrosion rate was the lowest under the optimal mixing ratios. XPS analysis revealed the existence of sulfur in the resin-ODT coating. The relatively high sulfur concentration was detected for the resin-ODT mix coating under the optimal mixing ratios.

Finally, it was clearly seen that the novel one-step process of resin-ODT mix coating had several advantages. It was very simple to apply such a coating continuously in the plant by just utilizing the existing facilities. Unlike pure resin, this new composition could produce a uniform, gray-colored film on EG steel. The coating should be thinner due to the dilution and had better

electrical properties. Most importantly, the corrosion resistance of this novel coating composition was significantly improved.

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