Hybrid Epoxy-silica Anticorrosive Coatings for Carbon Steel

J. Varela[1,2], V. Rodriuez-Lugo[2], E. Rubio[2] and V.M. Castano[3,*]

[1]Universidad Nacional Autónoma de México, Facultad de Química, Ciudad Universitaria, México D.F., México
[2]Centro Universitario de Vinculación, Benemérita Universidad Autónoma de Puebla,
Prolongación de la 24 sur y Av. San Claudio, sin número, Ciudad universitaria. Col. San Manuel. Puebla, Puebla 72570. México
[3]Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México,
Boulevard Juriquilla 3001, Querétaro, Querétaro 76230. México.

Abstract: *A series of hybrid coatings based on epoxy resin, tetraethoxysilane and coupling agent, were synthesized through a sol-gel technique and characterized by Fourier-Transformation Infrared (FTIR), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). Their corrosion protection effect was evaluated on cold rolled carbon steel (CRCS) coupons by performing visual analysis (ASTM test) and electrochemical measurements (electrochemical noise). The best performance anticorrosive was for the 75 wt% epoxy-25 wt% silica system in 5 wt% aqueous NaCl electrolyte. Enhancement of corrosion protection effect of the hybrids coatings may be due to the increase of the adhesion strength of the hybrid sol– gel coatings on CRCS coupons relative to pure epoxy, which was further evidenced by the measuring adhesion by tape test (ASTM D3359-02).*

1. INTRODUCTION

When exposed to the standard environment, most metals corrode through charge transfer reactions, which may cause deterioration occurring at the metal surface [1–2], leading to a considerable waste of resources [3]. Protective organic coatings are widely employed as a primer to protect steel surface from corrosion. However, poor adhesion of the coating material to the steel can cause not only delamination of the coating material, but also the corrosion of the steel substrate.

The Sol–gel process, has been used to prepare ceramer coatings to protect the metal surface from corrosion [4–6]. During the sol–gel process, metal alkoxides as sol–gel precursor produced a film as a barrier layer onto the metal substrate through the hydrolysis and condensation reaction. In the past decade, several reports have been dedicated to the corrosion protection of metals, by sol–gel derived organic–inorganic hybrids [7–9]. Actually, sol-gel coatings are used in commercial metal protection [10]. Silicon alkoxides are frequently used as sol–gel precursors, which function as both corrosion inhibitors and adhesion promoters. An organofunc-

tional group is necessary as an adhesion promoter between two different phases, namely the polymer coatings and the metallic surface.

To develop alternative novel advanced corrosion protection coatings, the adhesion strength of coating materials chemisorbed on various metallic substrates is a critical issue. Generally, organic/polymeric coating materials with poor adhesion to the metallic surface may lead not only to a delamination of the coating material, but also to the corrosion of the metallic substrate beneath the coating material. The effectiveness of the organic coating relied primarily on the interfacial adhesion strength between the metallic surface and polymeric coatings. Therefore, various silane coupling agents has been used as primers for increasing the corrosion protection effect of pure epoxy resin coatings, due to their enhancement of interfacial adhesion between the metallic surface and the polymeric coatings [11–16].

In this paper, we present the effective combination of the corrosion protection enhancing factors (i.e., adhesion promoting capability) into the hybrid coating system of as-prepared sol–gel materials and evaluate their corrosion protection effect on cold rolled carbon steel (CRCS) coupons by performing visual analysis
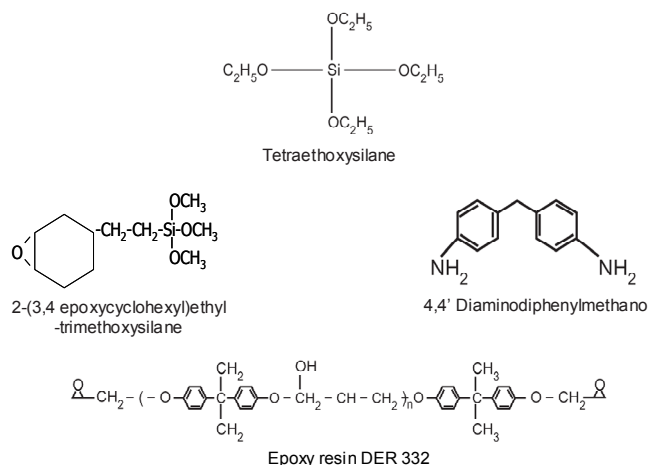
Figure 1. Epoxy-silica hybrid system precursors

(ASTM test) and electrochemical measurements (electrochemical noise). The observed enhancement of the corrosion protection effect of the hybrid sol–gel coatings may be due to the increase of the adhesion strength of the hybrid sol– gel coatings on CRCS coupons relative to pure epoxy, which was further evidenced by measuring adhesion by tape test (ASTM D3359-02).

2. EXPERIMENTAL

2.1. Materials

The organic phase of the hybrid was prepared by curing epoxy resin DER 332 (Sigma-Aldrich) with 4,4' Diaminodiphenyl-methane (DDM) from Fluka. As coupling agent, 2-(3,4 epoxycy-clohexyl)ethyl-trimethoxysilane (ECETMS) was employed. The inorganic phase precursor of the hybrid was tetraethoxysilane (Sigma-Aldrich), with ethanol as solvent and hydrochloric acid as catalyst, figure 1. As substrates, cold rolled carbon steel (CRCS) coupons were used.

2.2. Substrate preparation

The CRCS coupons, were washed and cleaned with detergent. In order to ensure a tight bond and good adhesion between the substrates surface and the sol-gel hybrid coating, the CRCS coupons were immersed in 5% wt NaOH solution at 60°C for 24 h and then rinsed with DI H_2O and acetone and dried to 60°C for 15 min.

2.3. Synthesis of epoxy-silica hybrid

The hybrid was prepared by sol-gel process with a two-stage process, as follows:

1. TEOS was prehydrolyzed by acidic catalysis of the mixture TEOS:ECETMS:H_2O-ETOH 0.8:0.2:1:2 molar, at room temperature for 1 h.
2. In the second stage, the prehydrolysed sol, was mixed with the organic component DER 332-DDM to start the "simultaneous" formation of both organic and inorganic polymer phases. In fact, the sol-gel process is faster and silica structures formed prior to the epoxy system. Mixtures were prepared to different weight % rates, as shown in table 1.

The dip coating method was used a rate of 10 cm/min. The coated CRCS coupons, were predried at room temperature for 24 h and cured at 125°C for 2 h. The coatings were analyzed by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR).

2.4. Electrochemical studies

Samples were immersed in a 5% wt NaCl solution at room temperature and removed for evaluation after 250, 500, 650 , 800, 950, 1150, 1400, 1750 h exposure. The panels were visually inspected according to ASTM D 610 (rusting degree) and ASTM D 714 (blistering degree), after which electrochemical noise (EN) analysis was carried out. The electrochemical noise is a very useful technique for the study of organic coatings and has been used in several reports [17–19]. EN measurements were undertaken using a three electrode system. The working electrodes (WE_1 and WE_2) were identically-coated samples with an exposure area of 1 cm^2. A saturated calomel electrode, was used as the reference electrode. The electrolyte was 5% wt NaCl at room temperature. The electrochemical noise measurements (ENM) were carried out with an electrochemical unit (Gill AC from ACM Instruments) coupled to a personal computer (PC), which was used to store data for further analysis, potential and current noise data being acquired simultaneously. The method consisted of measuring, as a function of time, the electrochemical potential noise (EPN) between the working electrode and the saturated calomel referenced electrode, and the electrochemical current noise (ECN) between the two working electrodes. In the EPN measurements the specimen was left at the open circuit potential (free corrosion potential). The ECN was obtained at the corrosion potential in the three electrode cell. This was achieved by using the electrochemical interface controlled by a PC, which also acted as a data logger/analyzer at a sample rate of one reading every second, as establish by Hladky and Dawson [20–21]. After gathering the data as a potential/current time record (time series) of 1024 readings, the DC drift was removed by subtracting a linear regression line from the data [22].

If both potential and current noise are measured, the standard deviation of potential can be divided by the standard deviation of current to obtain a value with units of resistance, known as the electrochemical noise resistance R_n. For noise resistance measurements the experimental arrangement shown in figure 2 was employed, using a coupled pair of working electrodes to measure the current noise, with the potential of this coupled pair being meas-

Table 1. Weight % rate epoxy-silica hybrid system

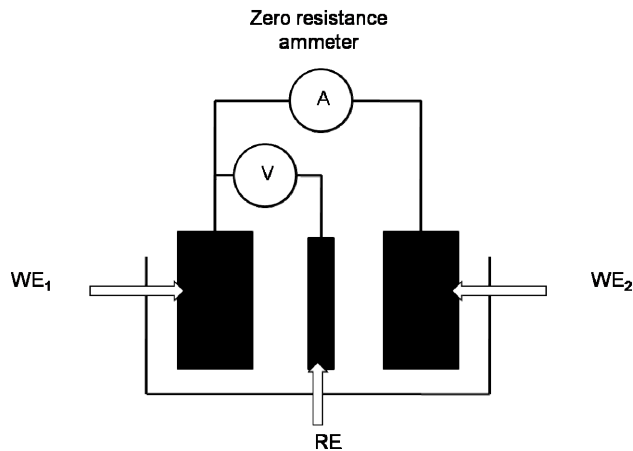| Sample code	Composition	
	Epoxy weigh %	Sol weight %
100-00	100	0
90-10	90	10
75-25	75	25
50-50	50	50
25-75	25	75
10-90	10	90
00-100	0	100

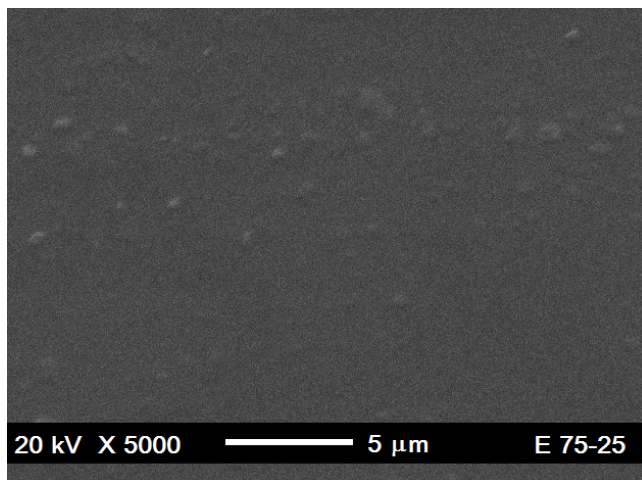Figure 2. Experimental arrangement cell

Figure 3. Micrograph of 75-25 hybrid coating.

Figure 4. Hybrid coating micrograph transversal section, (a) 75:25 and (b) 90:10 (epoxy:silica).

ured against a quite reference electrode.

2.5. Measuring adhesion by tape test (ASTM D 3359-02)

Adhesion strength by tape test was used to evaluate the adhesion of pure epoxy polymer and epoxy polymer-silica hybrid sol-gel coatings to the metallic substrate, according to ASTM D 3350-02. The typical procedure is as follows: first, the surface of the sample-coated was cut by a razor to make grid lines. The total test area was about 1 cm^2 with each square grid dimension of 1x1 mm. The Permacel 99 tape (a width of 25 mm, manufactured by Permacel) was applied firmly to cover the grid area of the coating at room temperature. After around 90 s, the Permacel tape was stripped off with one quick peeling. The adhesion strength of the coatings can be estimated by counting the number of squares peeled off as compared to the total number of squares.

3. RESULTS AND DISCUSSION

3.1. Scanning Electron Microscopy

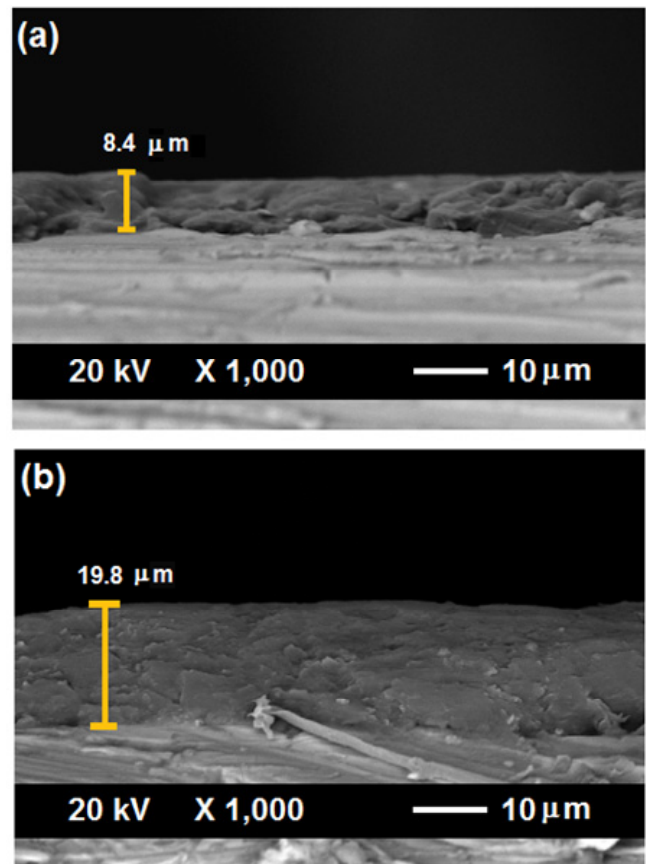Figure 3 shows a representative image of hybrid coating corre-

sponding to 75-25 epoxy-silica. According to figure 3, the inorganic particles were uniformly dispersed throughout the polymer matrix. These aggregates had a small size, less than 1 μm diameter and are embedded within the hybrid matrix. This result reveals that the hybrid coatings are uniform, and free of cracks. Figure 4 shows an SEM photograph of a cross section of coated CRCS coupons. It can be observed that the coating is well bonded and is free of defects such as surface blistering or cracks. The coating thickness measure on steel samples was ~8.4 μm, for the 75-25 epoxy-silica hybrid coating and ~19.8 μm, for 90:10 epoxy:silica hybrid coating.

3.2. Atomic Force Microscopy

As shown in figure 5 the hybrid sol-gel materials might have no organic-inorganic phase separation, indicating that the SiO_2 were dispersed in the epoxy matrix as shown in the SEM micrograph (figure 3). It exhibited good compatibility with the epoxy matrix for SiO_2 with ECETMS as coupling agent, but the larger silica loading (>50 wt %) would lead to an aggregation of silica particles. Therefore, the incorporation of low silica content (<50 wt %) into the polymer matrix may effectively enhance the smoothness of the surface [25,26].
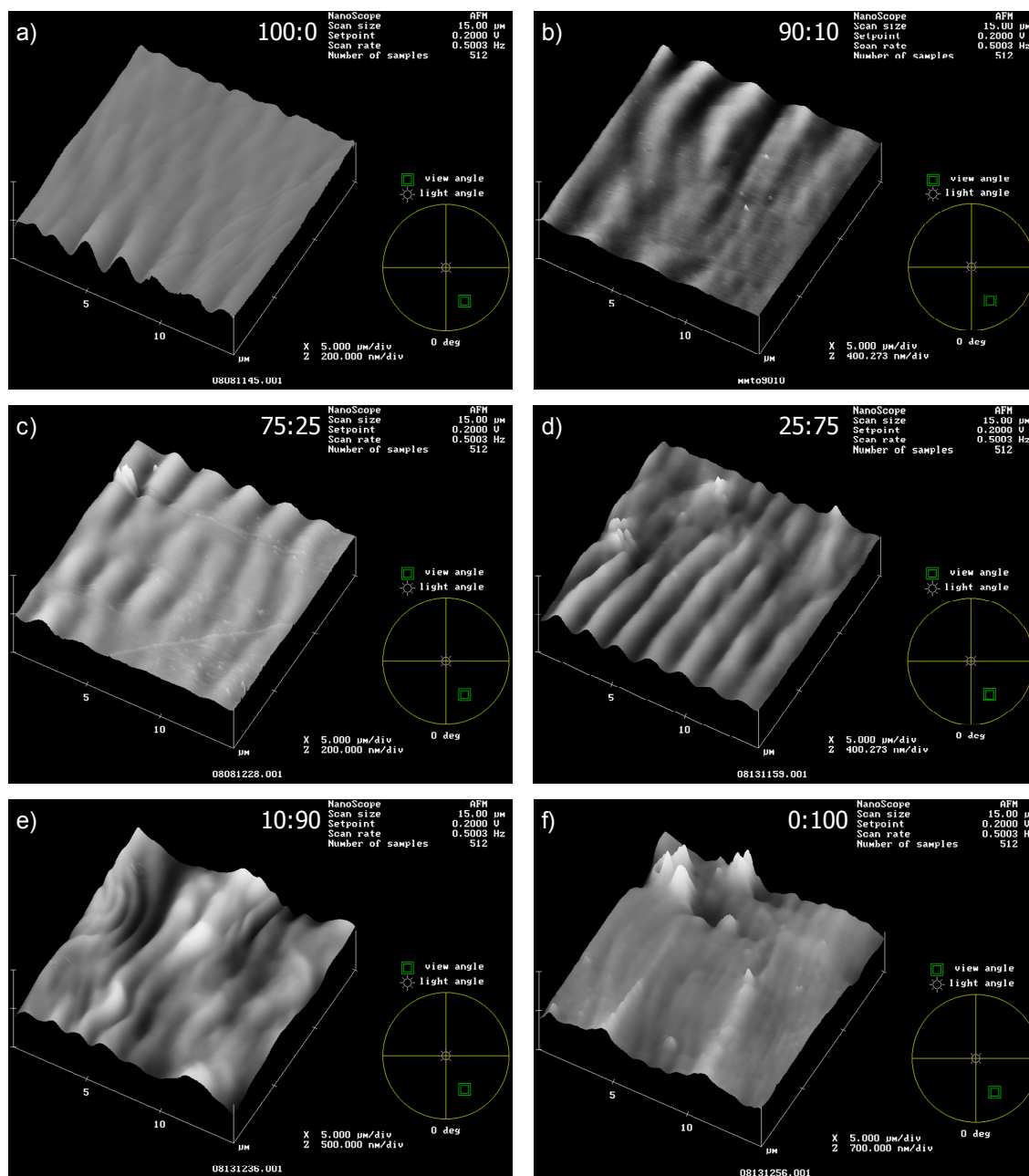
Figure 5. Hybrid coatings AFM micrographs on CRCS coupons.

3.3. Fourier Transform Infrared Spectroscopy

Figure 6 shows the FTIR spectra for ECETMS, silica, DER, and 50-50 hybrid. The FTIR absorptions bands of the ECETMS show the characteristic peak of the epoxy bonds at 912 cm^{-1}, the band at 1237 cm^{-1} is assigned to the ether bond in epoxide groups and the Si-O-C bond at 1081 cm^{-1}.

The FTIR absorption bands of the DER 332 are as follows: vibrations of groups CH$_3$ and CH$_2$ at 2967 and 2874 respectively, so others vibrations at 3053 are assigned to C-H bond relating to benzene ring, C=C vibrations for benzene ring, 1508 cm^{-1}, 1608 cm^{-1}. Absorption bands of epoxy groups are observed at 912 cm^{-1}, 862

cm^{-1}.

The FTIR spectra of the silica show characteristic vibration of Si-O bond at 793 cm^{-1} and 1082 cm^{-1}, while a vibration band observed at 953 cm^{-1} corresponding to Si-OH bond.

The characteristic peaks of hybrid 50-50 indicate the formation of Si-O bonds at 1072 cm^{-1}, and 952 cm^{-1}. The presence of the ethoxy group was found in all spectra by absorption bands of CH$_3$ and CH$_2$ at 2967 cm^{-1}, 2874 cm^{-1}, respectively. C=C vibrations for benzene ring at 1508 cm^{-1} and 1608 cm^{-1} were also observed.

FTIR spectra of hybrid also indicated the disappearance of the peak of epoxy group, instead, the absorption band of Si-O-C at
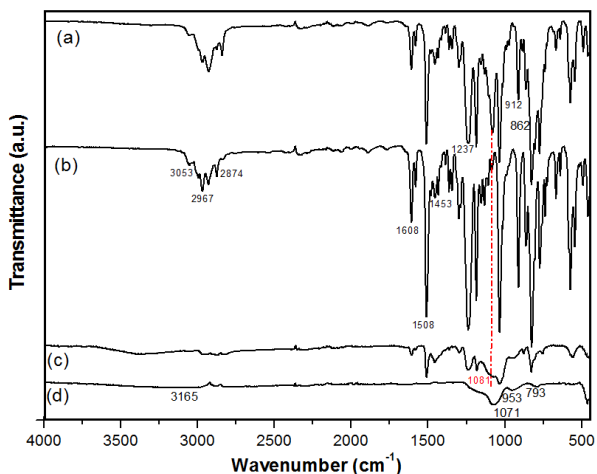
Figure 6. FTIR spectra of ECETMS (a), DER 332 (b), system 50-50 (c) and silica (d)

Figure 7. Noise resistance R_n as a function of exposure time in 5% wt NaCl solution

1081 cm^{-1} was observed, and these results indicate that covalent bonds are formed between inorganic and organic networks.

3.4. Electrochemical measurements

The results obtained to 5% wt NaCl solution after visual evaluation analysis of coated panels according to the ASTM D 616 and ASTM D 714 standards, are shown in tables 2 and 3 respectively. It
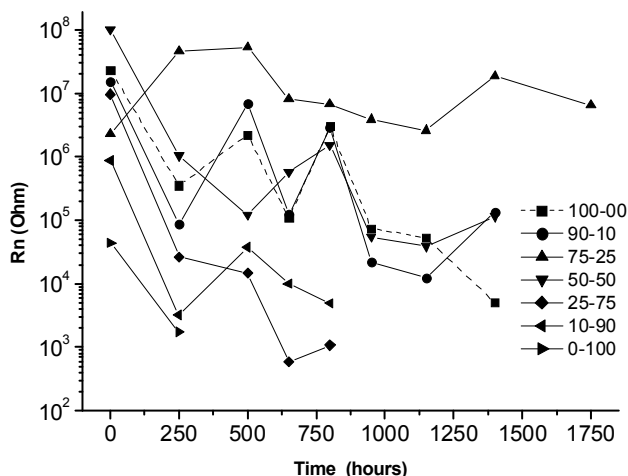
is clear that, the 25-75, 10-90, and 00-100 epoxy-silica hybrid coating fail before 250 h exposure to the 5% wt NaCl solution, while the 100-00 epoxy-silica hybrid coating fails after only 250 h exposure in the 5% wt NaCl solution, showing both blistering and rusting, whereas the other systems (90-10, 75-25 and 50-50 coatings) remain apparently undamaged (neither blistering nor rusting was

Table 2. Visual inspection analysis (ASTM D610)

Degree of rusting (ASTM D-610) after different exposure times in NaCl 5% wt for carbon steel panels covered with the epoxy-silica hybrid coatings.

Inmersion time, h	100-0	90-10	75-25	50-50	25-75	10-90	0-100	acero
250	10	10	10	10	8	7	5	5
500	9	10	10	10	8	4		
650	6	10	10	10	3	1		
800	2	10	10	10	2	1		
950	1	8	10	9				
1150	1	7	10	9				
1400	1	6	10	8				
1750			9					

Table 3: Visual inspection analysis (ASTM D714)

Blistering degree (ASTM D-714) after different exposure times in NaCl 5% wt for carbon steel panels covered with the epoxy-silica hybrid coatings.

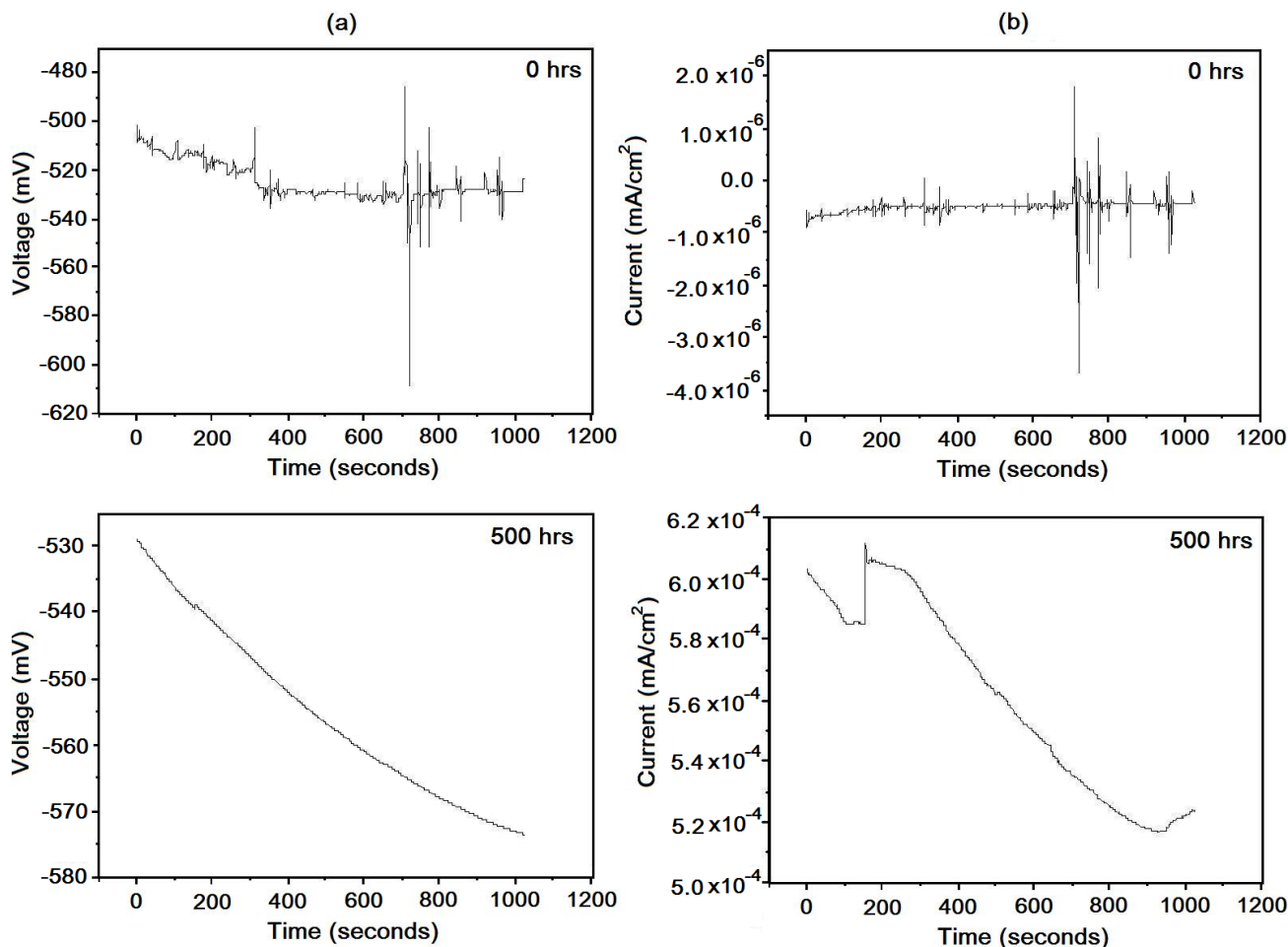| Iinmersión time, h	100-00	90-10	75-25	50-50	25-75	10-90	0-100
250	8F	8F	8F	8F	6F	8M	8M
500	8F	8F	8F	8F	6F	8M	
650	6F	8F	8F	8F	6M	8M	
800	6M	6F	8F	8F	6M	6F	
950	6D	6F	8F	8F			
1150	4D	6M	8F	6M			
1400	4D	6M	6F	6M			
1750			6F				

Figure 8. Potential noise records for exposure time indicated, system 100-00.

observed on the others coatings systems).

The behavior of R_n as a function of exposure time to 5% wt NaCl solution for the systems studied is shown in the figure 7. For the 100-00 epoxy-silica system, which failed on visual inspection after exposure for 250 h, the initial R_n values were found to decrease by two orders of magnitude after only 250 h. It then increased after 500 h and decline again after 650 h, then assuming very low values of 10^4 ohms beyond 950 h, thus providing a clear indication that this coating loses its anticorrosive properties. This behavior is probably due to the sealing of pores by corrosion products (showing a clear tendency to decrease with time), which means that corrosion has taken place at the metal/coating interface, in good agreement with the visual evaluation previously reported. Thus, the initial barrier effect disappeared in the 100-00 epoxy-silica system while in the other systems (90-10, 75-25 and 50-50) the effect was only attenuated.

With epoxy-silica coating systems 90-10 and 50-50, the initial values of R_n decreased by two orders of magnitude after 250 h, maintaining an average value of 10^5 ohms after 950 h until the end of the test.

The best performance was for 75-25 the epoxy-silica system, for which the initial R_n value increased by one order of magnitude after

250 h. It then decreased after 500 h and maintaining an average value of 10^7 ohms until the end of the test.

It is interesting to study the shape and magnitude of the current and potential noise transient signals. In figure 8 and 9 the potential-time and current-time series for the 100-00 and 75-25 systems at 0 h and after exposure for 500 h to 5% wt NaCl solution are shown. This exposure time was selected for the comparison because 100-00 system failed after this interval. In figure 8a, it can be seen that the potential noise values for 100-00 system are more noble at the beginning of the exposure (−500 mV to −550 mV versus SCE). For higher time of exposure (500 h), the corrosion potential decreases to more active values (between−530 and 575 mV). Note that in this figure, the longer the exposure time, (and consequently, the more degraded the coating), the lower are the amplitudes of the potential noise. For 75-25 system (figure 9a), the potential noise values at the beginning (between -490 and -520 mV) and at 500 h (between -430 and -495 mV) look very similar, even decrease, showing that system 75-25 has better anticorrosive properties than system 100-00. For the current noise values, system 100-00 shows signals that fluctuate more when the exposure time is longer. In addition, current noise values between 1 and -2.5×10^{-6} mAcm^{-2} were found during the stage of protection (0 h); between 6 and 5.2×10^{-4}
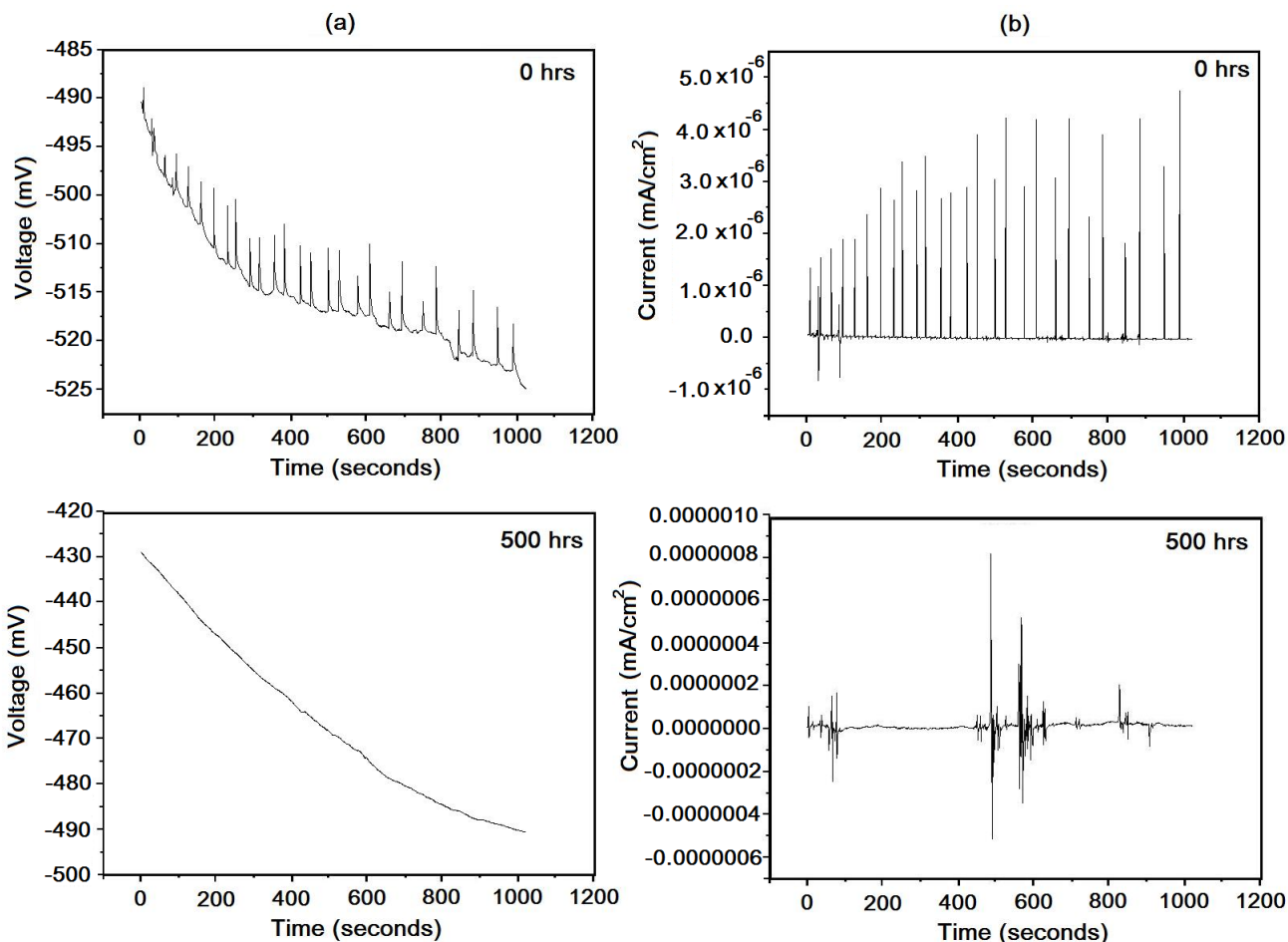
Figure 9. Potential noise records for exposure time indicated, system 75-25

mAcm^{-2}, for doubtful protection (500 h), as show in figure 8b, whereas, for the system 75-25, (figure 9b) the current noise values look very similar at 0 h (between 4×10^{-6} and 0 mAcm^{-2}) and at 500 h (between 6 and -4×10^{-7} mAcm^{-2}), showing better anticorrosive properties in good agreement with figure 7.

3.5. Measuring adhesion by tape test (ASTM D 3359-02)

In this study the measuring adhesion by test tape was used to examine the adhesion strength between the interface of polymer-silica hybrid coatings and carbon steel (CS) surface. The adhesion strength of epoxy-silica hybrid coatings to the surface was found to be much higher than the pure system epoxy coating alone as evidenced by the smaller stripped areas, as show in figure 10. The adhesion of the coating was further enhanced as the mount of the TEOS component was increased in the hybrid materials. It is particularly noteworthy that 90-10 coating showed a sufficient enhancement of adhesiveness (i.e. 17% of the area under the Permacel tape is peeled off). This percent was reduced to about 4% when the coating was a 50-50 hybrid material. As the TEOS content was increased to 75%, 90% and 100%, the hybrid sol-gel coating was intact when the tape was stripped off.
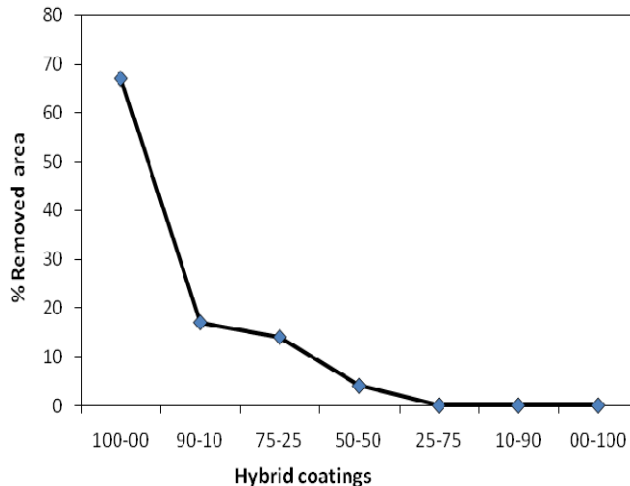

Figure 10. Measuring adhesion by tape test on epoxy polymer-silica hybrid sol-gel coatings according to ASTM D 3350

4. CONCLUSIONS

Continuous and crack free hybrid organic-inorganic epoxy-silica coatings were obtained onto a corrodible surface such as carbon steel by the sol-gel route.

Excellent agreement, has been observed between visual inspection analysis and electrochemical noise, which has been shown to be a useful tool for evaluating the anticorrosive performance of coatings.

The carbon steel treatment with NaOH, decrease % remove area as shown the adhesion measure by tpe test (ASTM D3359-02).

This paper show that sol-gel method is possible to synthesize hybrid coatings epoxy-silica with better corrosion resistance for carbon steel than neat polymer epoxy as demonstrate the obtain results for coating 75-25.

5. ACKNOWLEDGMENT

REFERENCES

[1] Denny AJ, "Principles and Prevention of Corrosion." Macmillan Publishing Company, New York, NY (1992).

[2] Mattsson E, "Basic Corrosion Technology for Scientist and Engineers." Second Edition, The Institute of Materials, London, UK (1996).

[3] Koch GH , Brongers MPH, Thompson NG, Virmani YP, Payer and JH, Corrosion Cost and Preventive Strategies in the United States , Report No. FHWA - RD - 01 - 156, Federal Highway Administration, U.S. Department of Transportation, McLean VA, March (2002).

[4] Wu KH, Chang TC, Yang CC, Wang GP, Thin Solid Films, 513, 84 (2006).

[5] Sang Il S, Jae HK, Kyung HC, Young YH, Surface & Coatings Technology, 200, 3468 (2006).

[6] Guglielmi M, J. Sol-Gel Sci. Tech., 8, 443 (1997).

[7] Nazanin F, Azam R and Amir EL, Iranian Polymer Journal, 14, 155 (2005).

[8] Wei-Gang J, Ji-Ming H, Liang L, Jian-Qing Z, Chu-Nan C, Surface & Coatings Technology, 201, 4789 (2007).

[9] Zheludkevich ML, Miranda I, Salvadob and Ferreira MGS, J. Mater. Chem., 15, 5099 (2005).

[10]Pagliaro M, "Silica-Based Materials for Advanced Chemical Applications" RSC Publishing, Cambridge (2009).

[11]Messaddeq SH, Pulcinelli SH, Santilli CV, Guastaldi AC, Messaddeq Y, Journal of Non-Crystalline Solids, 247, 164 (1999).

[12]Chou TP, Chandrasekaran C, Limmer SJ, Seraji S., Wu Y, Forbes MJ, Nguyen C, Cao GZ, Journal of Non-Cristallyne Solids, 290, 153 (2001).

[13]Ulf Bexell, T. Mikael Grehk, Surface & Coatings Technology, 201, 4734 (2007).

[14]Steven R. Davis, Adrian R. Brough, Alan A, Journal of Non-Crystalline Solids, 315, 197 (2003).

[15]Rubio E., Almaral J., Ramírez-Bon R., Castaño V., V. Rodríguez, Optical Materials, 27, 1266 (2005).

[16]Ying-Ling L, Wen-Lung W, Keh-Ying H, Wen-Hsuan H, Thermochimica Acta, 412, 139 (2004).

[17]Mabbutt S, Mills DJ, Woodcock CP, Progress in Organic Coatings, 59, 192 (2007).

[18]Mills DJ, Mabbutt S, Progress in Organic Coatings, 41, 39 (2000).

[19]De Rosa RL, Earl DA, Bierwagen GP, Corrosion Science, 44, 1607 (2002).

[20]Hladky K, Dawson JL, Corrosion Science, 21, 317 (1981).

[21]Hladky K, Dawson JL, Corrosion Science, 22, 231 (1982).

[22]Cottis R. and Turgoose S., "Electrochemical Impedance and noise." Corrosion Testing Made Easy Series (ed. B.C. Syrett), 68; Houston, NACE International (1999).