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## Effect of EtOH/H<sub>2</sub>O Ratio and pH on Bis-Sulfur Silane Solutions for Electrogalvanized Steel Joints Based on Anaerobic Adhesives

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*A minimum hydrolysis time is required to get an adequate crosslinking between a silane film and a metallic substrate and that depends on the contents of silane, ethanol, and water in the silane solution. The objectives for this work are: 1) to study the effect of different ratios of ethanol/water on the hydrolysis time for a 1% bis sulfur silane solution at pH 6, by attenuated total reflectance infrared spectroscopy. The different solutions studied correspond to different ratios of silane/ethanol/water by volume. The study was done following appearance of the siloxane and silanol groups and the disappearance of the ethoxysilane groups. 2) Also studied was the adhesion and corrosion behaviour of bis sulfur silane (bis[3 (bis[3 (triethoxysilyl)propyl]disulfide, DS) in solutions of ethanol/water at pH 4 and 6 and  $\gamma$  methacryloxypropyltrimethoxysilane (MPS) coatings obtained by a two step process on galvanized steel samples.*

*This coated surface was analysed by reflection absorption infrared spectroscopy (FTIR RA), scanning electron microscopy (SEM), and polarization curves. Results obtained at pH 6 were compared with the ones for pH 4. Single lap shear tests were used to contrast the behaviour of anaerobic adhesives on electrogalvanized steel silanized samples. It was observed that higher hydrolysis time was necessary to get good adhesion behaviour if the solution was prepared at pH 4, while at pH 6 the best behaviour was observed for short hydrolysis times.*

**Keywords:** Anaerobic adhesives; Coating; Silane

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## 1. INTRODUCTION

Several works have already proven that so-called bis-silanes or dipodal silanes provide metal surfaces with better protection than the so-called monopodal silanes, especially when combined with treatments including mono-silanes or monopodal silanes [1]. Zhu and van Ooij who tried to improve corrosion resistance on aluminium and galvanized-steel surfaces were the first researchers who worked on bis-silanes. Over-1% silane concentrations and different ethanol-water solutions were used for different kinds of silanes: bis-amino, bis-sulfur, and both combined [2]. The use of bis-amine silane is proven not to provide appropriate corrosion resistance due to its highly hydrophilic nature. The opposite was found for coatings based on hydrophobic silanes such as bis-sulfur. The main problem found in the use of this silane was the poor wettability of these silane solutions on certain surfaces such as zinc, as they formed films which provided an incomplete surface coating. The solution of this problem consists of the combined use of bis-sulfur and -amino coatings, which remarkably improved corrosion resistance on electrogalvanized-steel surfaces.

Poumi and Fagerholm [3] studied the suitability of using silane coupling agents to favour adhesion between paints and galvanized steel. The best results were obtained with a two-step method combining the treatment of a mono-silane on a bis-silane-treated surface.

Anaerobic adhesives are monocomponent systems extensively used in different fields such as automotive, aeronautics, electronics, etc., due to their capacity to retain cylindrical elements. Compatibility between these adhesives and silane coatings must be studied to ascertain if these kinds of coatings can effectively substitute traditional Cr (III) passivated coatings on electrogalvanized surfaces in applications demanding the use of anaerobic adhesives. These adhesives are oxygen-sensitive, diacrylate being their main component. Under oxygen-free conditions, the curing process takes place through free radical mechanisms [4,5]. This process is favoured by the presence of metallic cations such as those formed by iron. Iron and its alloys are well known to increase reaction kinetics, whereas cadmium or zinc, as well as synthetic materials or ceramics, are chemically inactive and require the use of a primer [6].

Previous works showed that the use of these types of silanes did not offer adequate corrosion behaviour on galvanized steel due to the fact that they provided non-homogeneous coatings. Nevertheless, no adhesion tests of these materials have been previously done; thus, the aim of this work was to achieve an enhancement of adhesion properties of electrogalvanized steel using anaerobic adhesives by means of bis-sulfur and MPS combined coatings.

## 2. EXPERIMENTAL PROCEDURE

The 95% purity silanes used were bis-(triethoxysilylpropyl) disulfide (DS) and  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS), provided by ABCR GmbH&Co KG (Karlsruhe, Germany). Deionised water was used for solution preparation and the pH was adjusted to 6 or 4 with 0.1 M acetic acid or with 0.1 M sodium hydroxide. The aqueous MPS silane solution was prepared at 1% by vol. and pH 4, under constant stirring. Hydrolysis of this MPS silane solution was studied by means of attenuated total reflectance infrared spectroscopy (FTIR-ATR) and  $H^1$ -NMR spectroscopies in previous works [7,8].

The DS solution was prepared at 1 vol. % silane at different silane/ethanol/water ratios at pH 6 (1/98/1, 1/49.5/49.5, 1/1/98). Hydrolysis of these DS silane solutions was studied by means of attenuated total reflectance spectroscopy (ATR) for different hydrolysis times. The ATR spectra were obtained using a Tensor 27 Fourier transform infrared (FTIR) spectrometer from Bruker (BrukerOptik GmbH, Madrid, Spain), equipped with a DuraSample Diamond accessory formed by a 0.5-mm diameter diamond embedded in a ZnSe crystal. Spectra were recorded with a resolution of  $4\text{ cm}^{-1}$  from  $4000$  to  $650\text{ cm}^{-1}$  and 32 scans were taken. Final spectra are the result of subtracting the water spectrum from the ethanol-water silane solution. In both cases, the background spectrum corresponds to the air spectrum at each considered time period. All spectra were normalized to the signal of  $1242\text{ cm}^{-1}$  ( $\text{CH}_2\text{-S}$ ) for better comparison [9]. Solutions with lower silane concentration are hard to follow-up by means of this technique, although better adhesion results can be obtained when used with another silane. For this reason, 0.5% solutions were used for silanization.

Using these data, electrogalvanized steel plates were silanized with a two-step process previously applied by Puomi and Fagerholm [3]. The samples including zinc coating were supplied by Finitec Electrolysis (Aranjuez, Madrid, Spain). They were cleaned with acetone in an ultrasonic bath for 5 mins and in an alkaline degreaser prior to silanization.

The two-step silanization process consists of the initial silanization of the electrogalvanized steel with the 24 h-hydrolysed DS silane solution by immersion for 10 min. Subsequently, the silanized specimens were left dry at room temperature for 10 min and silanized again with a MPS silane solution. After drying at room temperature for another 10 min, they were dried in an oven at  $110^\circ\text{C}$  for 60 min. The 1% MPS solution used is an aqueous solution at pH 4 and 150 min of hydrolysis which had been optimized in previous works [7].

The silanized-plate surface was analyzed by IR spectroscopy using the reflection-absorption infrared reflectance spectroscopy (RAIR) technique. The spectra were recorded with a resolution of  $4\text{ cm}^{-1}$  from 4000 to  $400\text{ cm}^{-1}$ , taking 128 scans at an angle of  $80^\circ$ . A degreased zinc-coated steel sample was used as a background.

Morphological changes of the samples were analysed by SEM measurements, using a Philips XL-30 microscope (Philips, Eindhoven, the Netherlands).

These samples were also used to study corrosion behaviour. The configuration of the electrochemical cell was based on the use of a reference saturated calomel electrode (SCE), a stainless-steel counter electrode, and, as a working electrode, the sample with the studied coating. A 263A potentiostat by EG&G Instruments Inc. Oakridge, TN, USA which features a programme for data management (352 SoftCorr III) was used. Tests were carried out at room temperature; corrosion potential ( $E_{\text{corr}}$ ) stabilization time was 10 min. The electrolyte used was a 0.6 M NaCl solution, with a sample exposed surface of  $1\text{ cm}^2$ , a scanning speed of  $1\text{ mV/s}$ , and an  $E_{\text{corr}}$  working potential of  $\pm 250\text{ mV}$ .

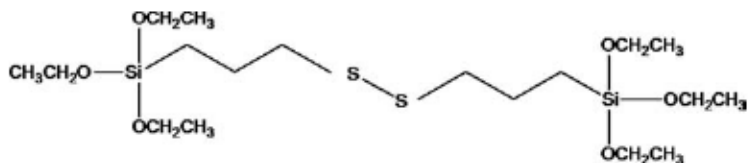
Finally, single lap shear tests were used to compare the strength of anaerobic adhesive joints on Zn-coated specimens both with and without silane surface treatment. The anaerobic adhesive used was Loctite<sup>®</sup> 638 (Henkel Technologies and Adhesives, Barcelona, Spain). This adhesive has a shear strength of 25 MPa (cured at  $25^\circ\text{C}$  for 24 hours) in the pin-and-collar test.

Adhesion tests were performed following the UNE-EN 1465 standard [10], with galvanized steel samples. Due to the characteristic of the anaerobic adhesives, the adhesive area was modified to  $1000\text{ mm}^2$  ( $40\text{ mm} \times 25\text{ mm}$ ) and the gap between substrates was  $50\text{ }\mu\text{m}$ . Metallic clips were used to obtain this gap. A universal machine provided with a 50 kN cell load was used to test the samples using a  $0.4\text{ mm/min}$  displacement rate. Mechanical tests were performed on 10 joints.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of Silane Solutions

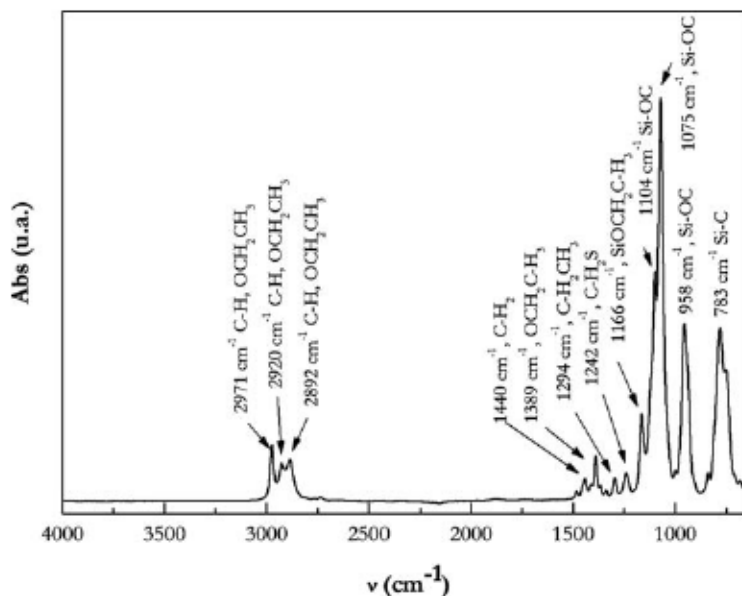
The structure of DS silane is shown in Fig. 1. The ATR spectrum of pure DS is shown in Fig. 2, where the bands have been assigned [11–16], are discussed next and are summarized Table 1. Thus, the presence of each of the studied silanes can be proven. This also facilitates the follow-up of the processes in which these bands are involved.



**FIGURE 1** Structure of the bis-(triethoxysilylpropyl) disulfide (DS).

The bands at 2971, 2920, and 2892  $\text{cm}^{-1}$  are assigned to C-H stretching in non-hydrolyzed ethoxysilane compounds ( $\text{SiOCH}_2\text{CH}_3$ ). The band at 1440  $\text{cm}^{-1}$  is associated with C-H bond strain in  $\text{CH}_2$ . The bands at 1398 and 1294  $\text{cm}^{-1}$  are associated with C-H stretching vibrations in the  $\text{CH}_2$  and  $\text{CH}_3$  in the ethoxy group ( $\text{SiOCH}_2\text{CH}_3$ ), respectively. The band at 1242  $\text{cm}^{-1}$  is assigned to C-H stretching in  $\text{CH}_2\text{-S}$ . The bands at 1166, 1104, 1075, 958, and 783  $\text{cm}^{-1}$  correspond to the stretching and strain modes of the ethoxysilane groups [17] ( $\text{SiOCH}_2\text{CH}_3$ ,  $\text{SiOC}$ ). All these bands except the one at 1242  $\text{cm}^{-1}$  must disappear as a result of DS hydrolysis.

Figure 3 shows the spectrum of a DS silane solution at 1% by volume and 1/98/1 silane/ethanol/water ratio at pH 6 for the region between



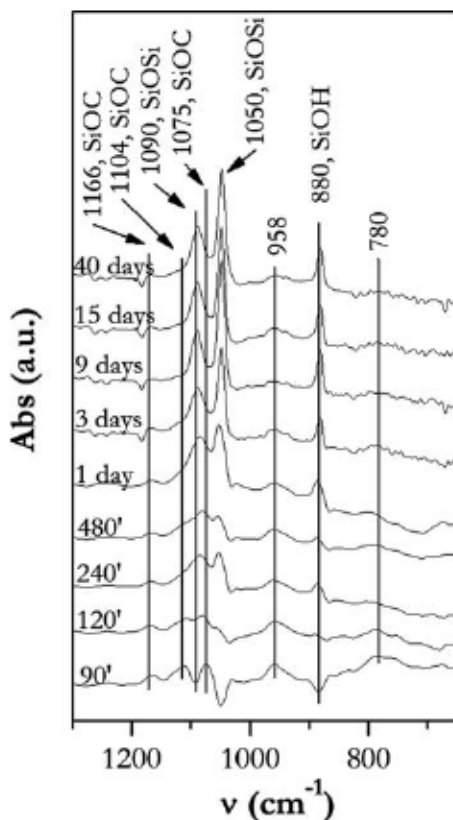
**FIGURE 2** The FTIR-ATR spectrum of pure DS.

**TABLE 1** Band Assignments for the FTIR-ATR Spectrum of DS and MPS Solutions and Their Respective Coatings on Galvanized Steel (The Bands in Italics Correspond to MPS and those in Bold Type can be Assigned to Both Silanes, While the Others Correspond to DS)

Band position (cm <sup>-1</sup> )	Assignments
2971	C H, SiOCH <sub>2</sub> CH <sub>3</sub>
2945	<i>C H, SiOCH<sub>3</sub></i>
2841	<i>C H, SiOCH<sub>3</sub></i>
2920	C H, SiOCH <sub>2</sub> CH <sub>3</sub>
2892	C H, SiOCH <sub>2</sub> CH <sub>3</sub>
1717	<i>C=O</i>
1638	<i>C=C</i>
1452	<i>C H, CH<sub>2</sub></i>
1440	<i>C H, CH<sub>2</sub></i>
1389	C H, SiOC H <sub>2</sub> CH <sub>3</sub>
1320	<i>C O C</i>
1296	<i>C O C</i>
1294	C H, SiOCH <sub>2</sub> C H <sub>3</sub>
1242	C H, C H <sub>2</sub> S
1190	<i>Si O C, SiOCH<sub>3</sub></i>
1166	<b>C-H, SiOCH<sub>3</sub>, and SiOCH<sub>2</sub>CH<sub>3</sub></b>
1104	<i>Si O C, SiOCH<sub>2</sub>CH<sub>3</sub></i>
1078	<b>Si-O-C, SiOCH<sub>3</sub>, and SiOCH<sub>2</sub>CH<sub>3</sub></b>
990 940	<b>Si-O-C, SiOCH<sub>3</sub>, and SiOCH<sub>2</sub>CH<sub>3</sub>.</b>
970 940	<b>Si-CH<sub>2</sub></b>
810	<i>Si O C, SiOCH<sub>3</sub></i>
780	<i>Si O C, SiOCH<sub>2</sub>CH<sub>3</sub></i>
470	<i>S S</i>
1130 and 1040	<b>Si-O-Si, cycle polysiloxane</b>
1090 1070	<b>Si-O-Si, (cycle siloxane)</b>
1090 and 1020	<b>Si-O-Si, lineal long chain of siloxane (higher crosslinker)</b>
1050	<b>Si-O-Si, lineal short chain of siloxane (lower crosslinker)</b>
1020 1010	<b>Si-O-Si, (cycle siloxane)</b>
~890	<b>SiOH</b>
~790	<b>Si-C, -(SiO)<sub>n</sub>-</b>
625 480	<b>Si-O-Si (dixiloxane)</b>

1330 and 650 cm<sup>-1</sup>. It can be observed that a new band due to SiOH hydrogen bonds appears at 880 cm<sup>-1</sup> when the time exceeds 90 min. Similarly, the bands at 1104, 1075, and 958 cm<sup>-1</sup> due to Si-OC vibrations in SiOCH<sub>2</sub>CH<sub>3</sub> disappear, leaving room for two new bands at 1090 and 1050 cm<sup>-1</sup> due to Si-O stretching in Si-O-Si. Therefore, the bands due to hydrolysis and condensation phenomena appear simultaneously.

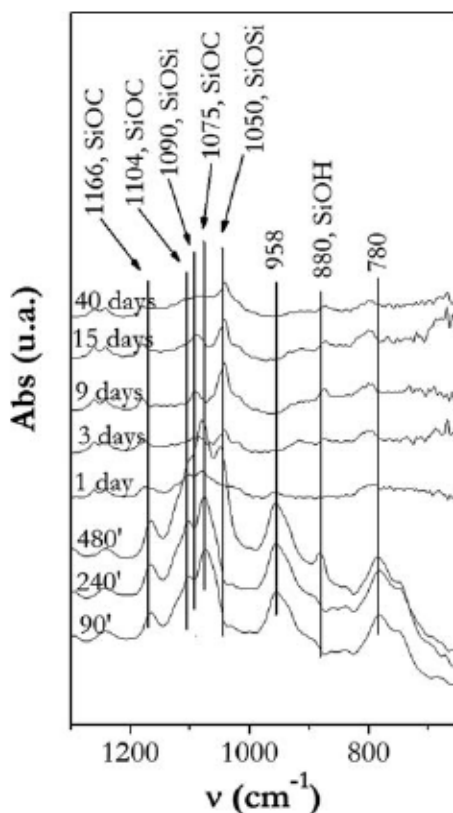
Increased intensity in the bands due to Si-OH and Si-O-Si vibrations is observed for longer hydrolysis times.



**FIGURE 3** FTIR-ATR spectrum of 1/98/1 silane/ethanol/water solution of 1% by vol. DS at pH 7.

Figure 4 shows the spectrum corresponding to the DS silane solution at 1% by vol. and 49.5/49.5 ethanol/water ratio at pH 6. It can be observed that equal water and ethanol content leads to a reduced hydrolysis rate relative to the 1/98/1 silane/ethanol/water solution. Thus, no disappearance of SiOC-related bands (1104, 1075, and  $958\text{ cm}^{-1}$ ) was observed within the first 24 hours of hydrolysis. At the same time, the appearance of bands at 1090 and  $1050\text{ cm}^{-1}$  due to Si-O stretching and at  $880\text{ cm}^{-1}$  due to Si-OH hydrogen bonds was also observed. However, their intensity is not comparable with that observed for the 98/1 ethanol/water solution. This may suggest that reduced ethanol/water ratio leads to reduced silane solubility. The intensity of the band at  $880\text{ cm}^{-1}$  does not grow with time because the condensation phenomena then taking place are more important

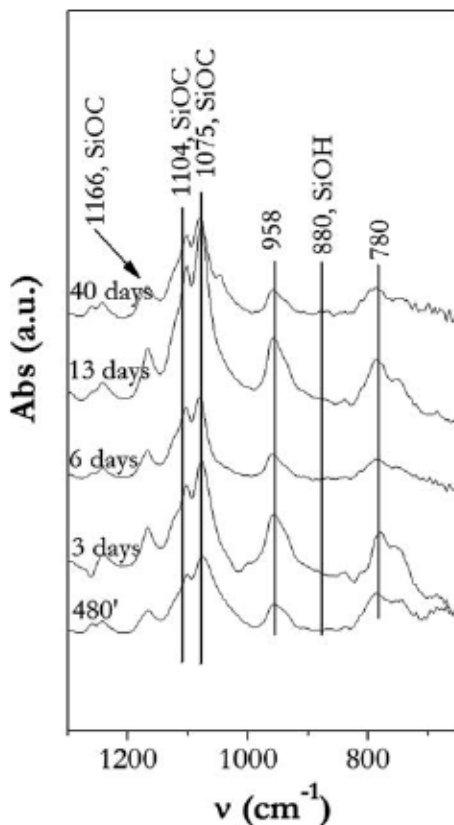




**FIGURE 4** FTIR-ATR spectrum of 1/49.5/49.5 silane/ethanol/water solution of 1% by vol. DS at pH 7.

than hydrolysis phenomena. From the fifteenth day of hydrolysis, widening is observed at  $1100\text{--}1000\text{ cm}^{-1}$  as condensation progressively gains importance.

Figure 5 shows the FTIR spectra of the 1% by vol. DS and silane/EtOH/H<sub>2</sub>O (1/1/98) ratio at pH 6. From the observation of signals located at 1166, 1104, 1075, and  $958\text{ cm}^{-1}$  (corresponding to SiOC groups), it can be confirmed that no progress of the hydrolysis reaction occurs for such elevated water contents. No advance in the hydrolysis process is observed within the studied time period for such high water content, since the bands at 1166, 1104, 1075, and  $958\text{ cm}^{-1}$  do not disappear during the time period studied and the appearance of no new bands due to hydrolysis or condensation phenomena is observed. Increased intensity is observed in these bands due to nonhydrolyzable



**FIGURE 5** FTIR-ATR spectrum of 1/1/98 silane/ethanol/water solution of 1% by vol. DS at pH 7.

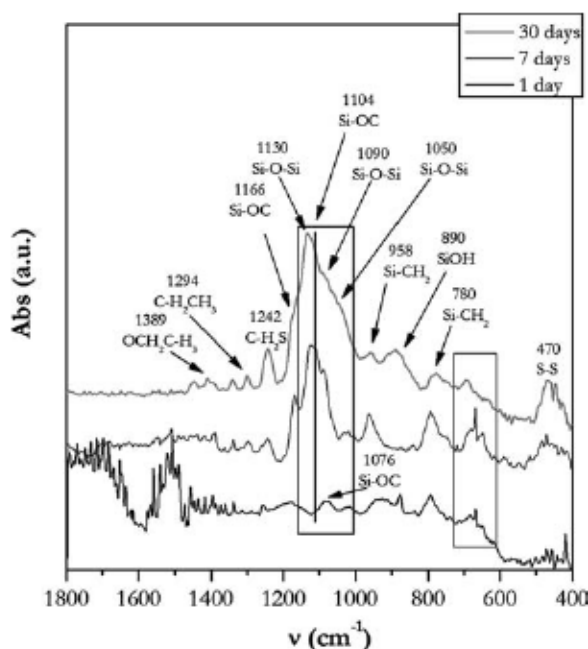
groups (ethoxy groups); this may be due to increased solution “stability” as hydrolysis time rises. Besides, this seems coherent with that observed in the prepared solution, where large silane drops (insoluble in ethanol/water) were initially observed. As time elapses and the solution is kept under continuous shaking, silane drops split up into smaller ones. This may lead to a far more homogeneous solution and may also justify the increased intensity observed, in spite of the fact that no advances were observed, in the silane hydrolysis process.

### 3.2. Surface Characterization of Silane Films

On the basis of the data obtained from the studied solutions, it was decided to use a high ethanol-content solution to silanize the

electrogalvanized-steel substrates, as the other two solutions provide far slower hydrolysis rates. A 0.5% by vol. silane solution (0.5% below that used to study hydrolysis) was used to favour adhesion. The first step is to check if the silane film has settled on the electrogalvanized steel. Reflection absorption infrared spectroscopy (FTIR-RAIR) was one of the techniques used to study this. Figure 6 shows the spectra corresponding to the electrogalvanized surfaces with DS silane films at pH 6, and Fig. 7 corresponds to the electrogalvanized surfaces with coating DS (at pH 6) + MPS (see Section 2). In addition, these surfaces were studied by SEM (Fig. 8). These results will be compared with the ones obtained for the DS solution at pH 4 (Fig. 9).

Figure 6 refers to the spectra on electrogalvanized steel coated with 0.5% by vol. DS in silane/ethanol/water (0.5/99/0.5) at pH 6 for different hydrolysis times (1, 7, and 30 days) and shows all DS silane-related bands. Given the low intensity of these bands, it seems rather clear that there is still little silane on the surface and that the bands due to nonhydrolyzed groups ( $\text{SiOCH}_2\text{CH}_3$ ) can be observed at



**FIGURE 6** FTIR-RA spectrum of an electrogalvanized surface coated with 0.5% by vol. DS in ethanol/water solution at pH 7 for the 0.5/99/0.5 silane/ethanol/water ratio and different hydrolysis times (1, 7, and 30 days).

1166 and 1076  $\text{cm}^{-1}$ . The presence of this small amount of silanol groups in the solution has allowed reaction with the electrogalvanized steel. This is proven by the appearance of bands within the 700–600  $\text{cm}^{-1}$  region (framed in grey in the graph) that could be attributed to SiOZn [7] or disiloxane (SiOSi) [13,14] bonds. In both cases the result is the same; the crosslinking increases with the time, so the amount of silane on the surface increases also. This agrees with what is shown in Fig. 3 for the hydrolysis of this solution, where the bands corresponding to ethoxysilane groups ( $\text{SiOCH}_2\text{CH}_3$ , at 1104 and 1076  $\text{cm}^{-1}$ ) which have not been completely hydrolyzed can be observed after 1 day of hydrolysis. Besides, the hydrolysis ( $\text{SiOH}$  at 890  $\text{cm}^{-1}$ ) and condensation ( $\text{SiOSi}$  at 1090 and 1050  $\text{cm}^{-1}$ ) bands begin to appear.

The presence on the surface of electrogalvanized steel of the band at 890  $\text{cm}^{-1}$ , associated with silanol groups ( $\text{SiOH}$ ), is due to the fact that not all silanol groups formed during hydrolysis have condensed on the surface. Also, the water released as a result of the condensation of silanol groups ( $\text{SiOH}$ ) can be employed to hydrolyze ethoxysilane groups. Ethoxy groups, in the presence of this condensation water, hydrolyze, thus, giving rise to new silanol groups [11].

Increased intensity is observed in all bands when hydrolysis time rises (7 days) due to the larger amount of silane on the electrogalvanized steel. This fact is corroborated by the increased intensity observed in bands related to vibrations non-related to hydrolysis and condensation processes (*i.e.*, those containing sulphur and appearing at 1242 and 470  $\text{cm}^{-1}$ :  $\text{C-H}_2\text{S}$  and  $\text{S-S}$ , respectively). Furthermore, grey-framed bands within the 700–600  $\text{cm}^{-1}$  region and related to the electrogalvanized steel-silane binding also seem to show slightly increased intensity. This indicates the presence of an increased amount of silane on the surface. All this can be explained by the increase of thickness intensity in the silane film. Therefore, the increase in the band at 1166  $\text{cm}^{-1}$  related to nonhydrolyzed bonds ( $\text{SiOC}$ ) need not be due to an increased amount of ethoxy groups in the solution, but to the increased amount of silane on the surface. This leads to greater absorption in these bands ( $\text{Si-OC}$ ).

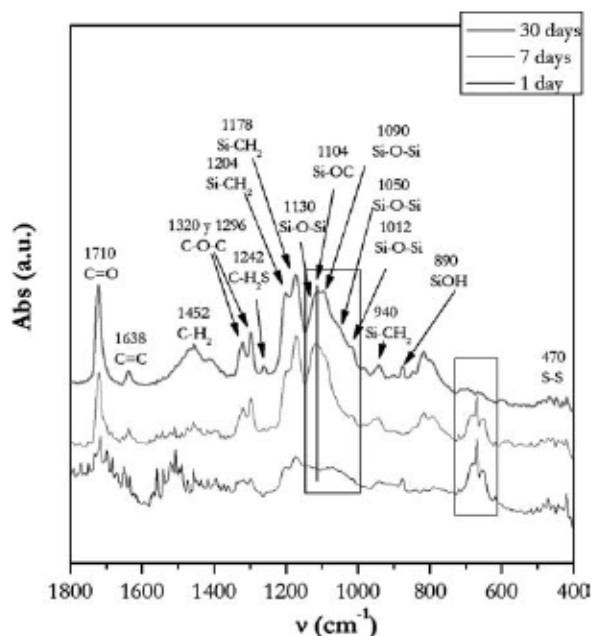
The condensation bands within the 1150–1000  $\text{cm}^{-1}$  region (framed in black), which were associated with the bands corresponding to siloxane bonds, are those undergoing greater change. Strongly increased intensity is observed in the bands at 1130, 1090, and 1050  $\text{cm}^{-1}$  due to siloxane bonds. The increased amount of siloxane and silane-zinc bonds should lead to water release and, therefore, increased intensity should then be observed in the band at 890  $\text{cm}^{-1}$  (due to  $\text{SiOH}$  bonds) as a result of the afore mentioned hydrolysis process, undergone by

ethoxysilane groups present at the surface, with condensation water. However, this band is scarcely visible for 7 days of hydrolysis. The absence of this band can be justified by the fact that this condensation-related water is indeed being consumed in the formation of silanol groups, which may be condensing quickly with other close silanol groups or the electrogalvanized steel itself. This is the reason behind this remarkably high number of condensation bands. This may not apply for 1 day of hydrolysis, since the number of nonhydrolyzed groups in the solution is far lower, as can be observed in Fig. 6.

The amount of silane on the electrogalvanized steel increases for higher hydrolysis times (30 days). This effect is confirmed by the increment of intensity observed in the bands at 1242 and 470  $\text{cm}^{-1}$  (C-H<sub>2</sub>S and S-S, respectively) as shown in Fig. 6. The 1150–1000  $\text{cm}^{-1}$  region undergoes widening, this producing overlapping among the different condensation bands, thus leading to the conclusion of greater silane-film crosslinking. Decrease of signals within the grey-framed 700–600  $\text{cm}^{-1}$  region confirms it. The increased intensity in the band at 890  $\text{cm}^{-1}$ , associated with silanol groups, is due to the hydrolysis of the ethoxysilane groups in the film with the water released from condensation phenomena, thus giving rise to these silanol bonds. Due to the higher crosslinking in the silane film, newly generated silanol groups are very likely to be far from one another and from the surface. This situation hinders condensation among these newly created silanol groups. Thus, they are not observed after 7 days of hydrolysis but after 30.

Figure 7 shows the spectrum corresponding to the electrogalvanized steel coated with the 0.5% DS silane film in silane/ethanol/water (0.5/99/0.5) at pH 6, and, subsequently, coated with 1% MPS solution in water at pH 4 by means of the two-step process. Many of the bands observed at the surface coated only with the DS silane overlap with the bands of the MPS silane when both are coating the galvanized steel, especially in the condensation area. The presence of the MPS film is, therefore, completely proven by the presence of the bands at 1710, 1638, 1320, and 1296  $\text{cm}^{-1}$ , which characterize the MPS film, for the vibrations corresponding to C=O, C=C and C-O-C bonds, respectively. Besides, a reduction is observed in DS silane-related bands such as those at 1242 and 470  $\text{cm}^{-1}$  (corresponding to C-H<sub>2</sub>S and S-S bonds, respectively). This would justify the presence of the MPS silane film over the DS silane film.

In Fig. 7, as in the previous case (see Fig. 6), for 1 day of hydrolysis of the DS solution, the intensity of the bands corresponding to silane films is lower than for higher hydrolysis times. When samples are coated with MPS, two new bands corresponding to SiCH<sub>2</sub> bonding, located at 1204 and 1178  $\text{cm}^{-1}$ , arise.



**FIGURE 7** FTIR-RA spectrum of an electrogalvanized surface coated by means of the two-step process with: a) 0.5% by vol. DS silane solution in ethanol/water solution at pH 7 for the 0.5/99.0.5 silane/ethanol/water ratio and different hydrolysis times (1, 7 and 30 days), and b) 1% by vol. MPS silane solution in 100% water solution at pH 4 hydrolysed for 150 min.

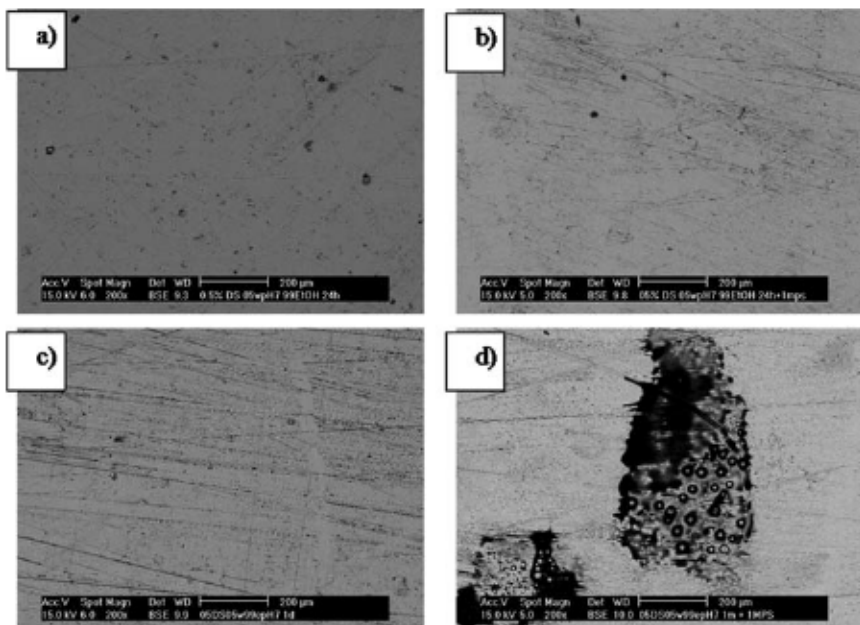
Increased intensity in the bands related to both silanes (Fig. 7) was observed for 7 days of hydrolysis of the DS solution and 150 min of hydrolysis of the MPS solution as a result of the presence of a larger amount of both films on the surface. In Fig. 6 (DS-only film for different hydrolysis times), this increase of the film settled on the electrogalvanized steel is due to the higher number of siloxane bonds (SiOSi) in the DS solution and the increase in the number of SiOH groups in this solution. Increased numbers of silanol groups lead to increased number of siloxane bonds during the oven-curing process of both films, due to the condensation phenomena among silanol groups from the same silane and to condensation phenomena among silanol groups from both silanes.

A new band close to  $820\text{ cm}^{-1}$  appears for 7 and 30 days. It could be related to the Si-C bond when Si is part of siloxane bonds  $(\text{-Si-O})_n\text{-}$  [12]. It seems possible since a similar increase is observed in the band at  $780\text{ cm}^{-1}$ , also associated with Si-C bonds.

As for the film formed with the DS solution only, the intensity of (black-framed) condensation bands increases and the intensity of bands at  $700\text{--}600\text{ cm}^{-1}$  (grey-framed) decreases as hydrolysis time increases. Both effects can be explained by the increased amount of the silane film settled on the electrogalvanized steel as a consequence of greater crosslinking among SiOH groups when their number increases as hydrolysis time rises.

These same coatings prepared from DS solutions in water at pH 4 both with and without MPS give rise to spectra very similar to those obtained at pH 6 (graphs are not shown for this reason). In coatings with DS only, the highest differences were observed for 1 day of hydrolysis, since most bands show higher intensity for the film formed from water at pH 4. This may show a greater presence of silane on the surface. This idea would be supported by the increased intensity observed in the bands related to both siloxane and silane-metallic surface (SiOZn) bonds. This can be due to the higher number of bonds between the silane film and the surface as a consequence of the higher hydrolysis rate in this solution. This would mean a higher number of SiOH groups for the same hydrolysis time than for the solution prepared from water at pH 6. As time elapses, increase in condensation band intensity occurs. The trend is the same when both coatings (DS and MPS) are present.

By way of example, Fig. 8 shows two micrographs corresponding to the electrogalvanized-steel surface treated with 0.5% DS in silane/ethanol/water (0.5/99/0.5) at pH 6 for 1 day of hydrolysis (a) without subsequent treatment with MPS and (b) with the two-step process (DS + MPS). As shown by micrograph (a), no silane deposits can be observed on specific surface areas. Energy dispersive X-ray (EDX analysis) shows how thin the DS film must be, since the weight percentage of Si and S is quite low and this measurement involves great error. Subsequent MPS treatment of this surface [micrograph (b)] shows the percentage of similar S and slightly higher Si, thus supporting the presence of MPS on the surface. Darker areas, corresponding to silane deposits (specifically MPS) are observed (by EDAX) on this surface, where Si weight reaches 52.06% in some areas, while it is 1.88% in the remaining surface. Therefore, the MPS film seems not to be homogeneously distributed over the DS-coated surface. Figure 9 shows the same study for the DS solution prepared with water at pH 4. Although micrograph (a) shows no silane deposits on specific surface areas, a slightly more intense shade of colour can be made out in extensive surface areas. However, EDAX analysis shows no significant differences among these areas. It is rather clear that the percentage of Si on the whole surface is higher than that observed at pH 6 (around

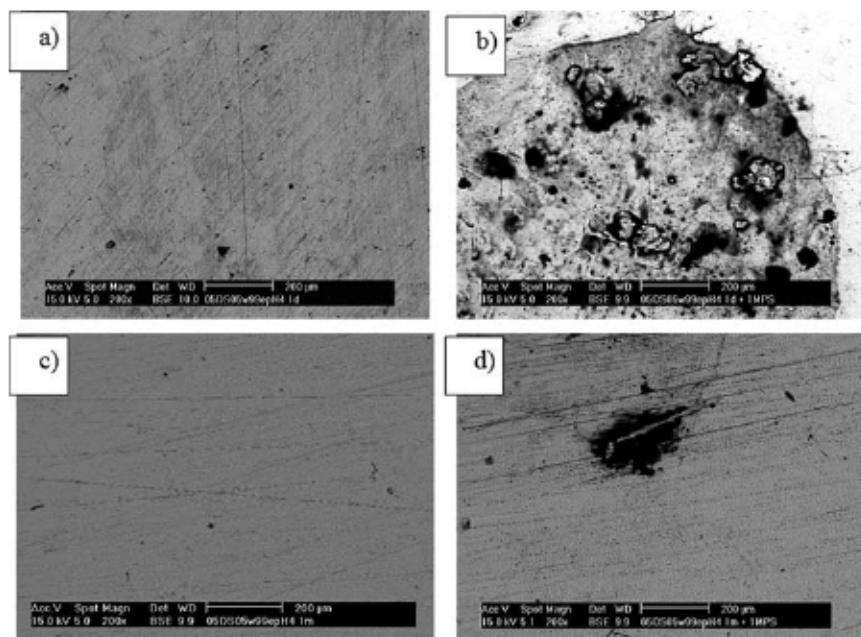


**FIGURE 8** SEM micrograph of an electrogalvanized surface a) coated with 0.5% by vol. DS ethanol/water pH 6 for ratio DS/ethanol/water 0.5/99/0.5 and 1 day of hydrolysis, b) additionally coated with the DS at pH 6 and MPS solutions by means of the two-step process for 1 day of hydrolysis of the DS solution, c) same as 'a' for 30 days of hydrolysis, and d) same as 'b' for 30 days of hydrolysis.

1.23%). When this surface is treated with MPS [micrograph (b)], as in the previous case, the percentage of Si on the surface increases, even up to reaching 60.74% in the darkest areas. Therefore, as occurred with pH 6, MPS is not homogeneously distributed over the DS surface.

By way of example, Figs. 8 and 9 show two micrographs corresponding to the electrogalvanized-steel surface treated with the 0.5% DS in silane/ethanol/water (0.5/99/0.5) at pH 6 and 4 for 30 days of hydrolysis without subsequent MPS-solution (Fig. 8c and 9c) or with the two-step process (DS + MPS) (Figs. 8d and 9d) treatment. As can be observed in micrographs Figs. 8c and 9c, the surface is still rather homogeneous and no silane deposits can be observed on specific surface areas. In the case of the film at pH 6, EDAX analysis shows higher Si percentages than those observed for 1 day of hydrolysis. Therefore, the DS film must be thicker as a consequence of its greater crosslinking, as supported by FTIR-RA analysis. Thus, the values of Si and S





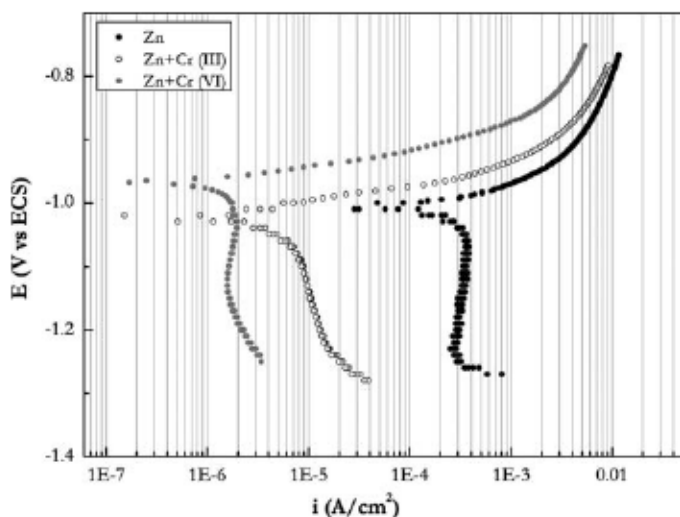
**FIGURE 9** SEM micrograph of an electrogalvanized surface a) coated with 0.5% by vol. DS ethanol/water pH 4 for ratio DS/ethanol/water 0.5/99/0.5 and 1 day of hydrolysis, b) additionally coated with the DS at pH 4 and MPS solutions by means of the two-step process for 1 day of hydrolysis of the DS solution, c) same as 'a' for 30 days of hydrolysis, and d) same as 'b' for 30 days of hydrolysis.

are approximately 1.61 and 1.38%, respectively. Micrographs with greater magnification show DS accumulations in the sanding marks (9.76% Si and 8.96% S). In the micrograph in Fig. 9c for the DS film at pH 4 the values of Si and S weight are approximately 1.88 and 1.58%, respectively. These figures are slightly higher than those observed at pH 6. In this case, micrographs with greater magnification also show DS accumulations in sanding marks (9.06% Si and 7.82% S). Subsequent MPS treatment of these surfaces (Fig. 8d: pH 6) shows the percentage of similar S and slightly higher Si, thus supporting the presence of MPS on the surface. In this case, darker areas corresponding to silane deposits (particularly MPS) can also be observed. Si reaches 23.73% in the darkest areas and 0.89% in the lighter ones. Therefore, the MPS film is not homogeneously distributed on the DS-coated surface. The same occurs with Fig. 9d for the DS solution at pH 4. Si reaches 60.47% in the darker areas and 1.17% in the lighter ones.

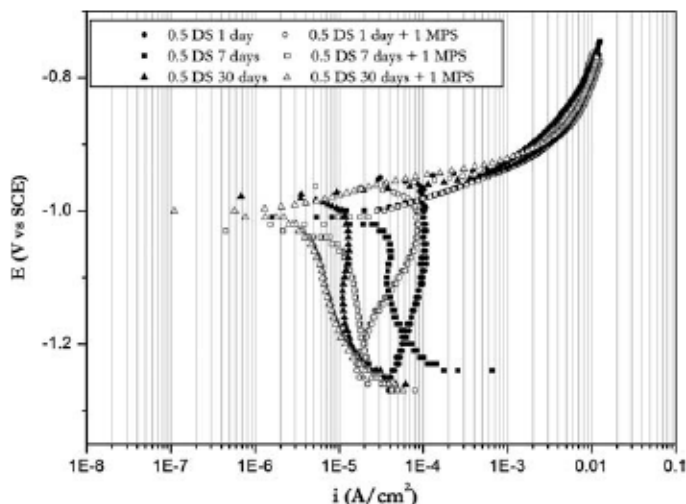
### 3.3. Corrosion Test

Figure 10 shows the polarization curves corresponding to chromeless electrogalvanized-steel, with Cr (III) and Cr (VI). The current density significantly diminishes in the presence of chrome. This reduction of the current density of the electrogalvanized steel reaches up to two orders of magnitude in the case of Cr (VI) passivation, thus increasing steel protection.

Figure 11 shows the polarization curves obtained on electrogalvanized steel surfaces treated with 0.5% DS in silane/ethanol/water (0.5/99/0.5) at pH 6 for different hydrolysis times (1, 7, and 30 days) both with and without subsequent coating with 1% MPS in water at pH 4 and 150 min of hydrolysis. The density of the cathode current decreases slightly after DS treatment, with respect to the electrogalvanized steel without silane. Moreover, this reduction grows as the hydrolysis time of the silane solution elapses. The presence of both coatings (DS + MPS) on the electrogalvanized-steel surface leads to the displacement of the polarization curves towards lower current densities relative to the curves for surfaces with DS only. In the particular case of the cathode branch, the reduction of the current density is higher than that observed in the anode branch. Nevertheless, the trend is still the same: the current density grows smaller as the hydrolysis time of the DS silane solution increases. The silane film



**FIGURE 10** Polarization curves in 0.6M NaCl solution of chromium-free electrogalvanized steel coated with Cr(III) and Cr(VI).



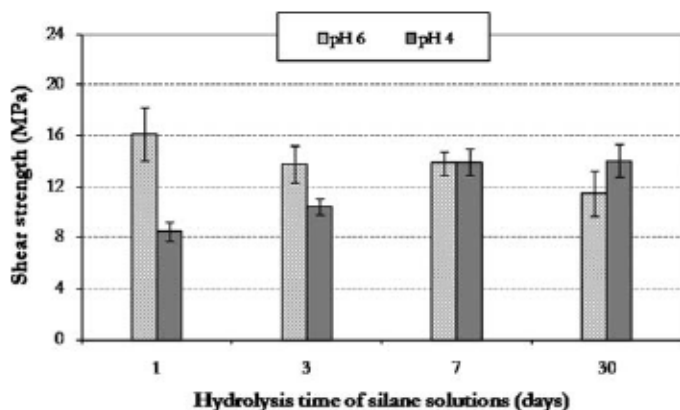
**FIGURE 11** Polarization curves in 0.6M NaCl solution of electrogalvanized steel coated with a 0.5% by vol. DS silane solution in the 0.5/99/0.5 silane/ethanol/water ratio at pH 7 and hydrolyzed for 1, 7, and 30 days both with and without subsequent coating: a 1% by vol. MPS solution in 100% water at pH 4 for 150 min of hydrolysis.

practically inhibits the cathodic process, since it may be acting as a barrier for  $O_2$  to reach the metal. Therefore, the anode branch remains practically the same. Although the reduction of the current density is not as significant as in Cr coatings, a reduction is observed when both silanes are used for coating.

The curves obtained from the DS solutions at pH 4 both with and without MPS coating render very similar results.

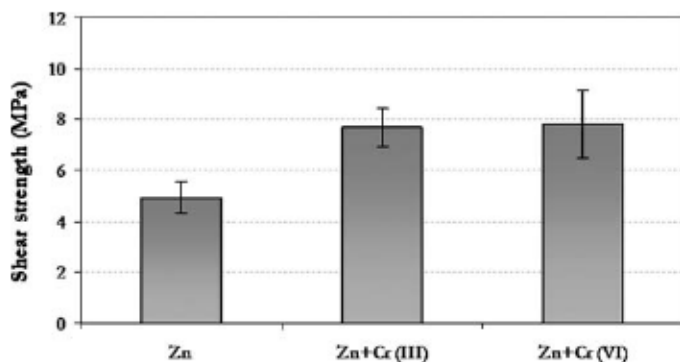
### 3.4. Mechanical Test

To compare the results obtained by FTIR-RA and the corrosion test, single lap shear samples were silanized for different hydrolysis times (1, 7, and 30 days) and pH (4 and 6) of the DS silane solutions. Results are shown in Fig. 12. In addition, these results obtained for silanized samples were compared with electrogalvanized samples both with and without passivation Cr (III and VI) (see Fig. 13). The comparison of the results of electrogalvanized samples (Zn) both with and without silane shows that the use of DS+MPS coatings (two-step process) on electrogalvanized-steel leads to increased bonding strength. For 1 day of hydrolysis, the highest results are those obtained for surfaces



**FIGURE 12** Average shear strength (single lap shear test) for anaerobic adhesive joints made of electrogalvanized steel samples [without Cr(VI)] treated with silane solutions in a two-step process: 1) 0.5% by vol. DS in silane/ethanol/water (0.5/99/0.5) at pH 7 or 4 for 1 day of hydrolysis, and 2) 1% by vol. MPS at pH 4 for 150 min of hydrolysis.

prepared from the DS solution at pH 6. As hydrolysis time elapses, the shear strength of these bonds decreases. However, the obtained values always exceed those obtained for nonsilanized chromeless and Cr (III and VI) bonds. Shear strength in bonds prepared from the DS solution at pH 4 for 1 day of hydrolysis are far lower than those obtained for pH 6. However, as hydrolysis time elapses, their shear strength increases.



**FIGURE 13** Average lap shear strength (single lap shear test) for anaerobic adhesive joints made of Zn-coated specimens with different surface treatments: electrogalvanized steel samples both with and without Cr(III and VI) passivation.

Obtaining lower shear strength values at pH 4 may be a consequence of the greater thickness of the silane film, as previously pointed out. This greater thickness may well not involve large-enough crosslinking among silanol groups to avoid movements between the silane chains, which would then render lower resistance values. The number of siloxane (SiOSi) bonds in the solution at pH 4 increases as hydrolysis time elapses, thus maintaining a high number of silanol groups and, hence, giving rise to a high number of galvanized steel bonds (SiOZn) and a film with greater crosslinking. This may hinder movement between the different silane chains.

In bonds formed from the solution at pH 6, resistance reduces as time elapses, although it always exceeds that obtained for Cr (VI) passivated coatings, and equals or improves that obtained at pH 4. This reduction may be justified by the lower number of silanol groups in the solution as time elapses, since they are forming siloxane groups.

Single lap shear specimens showed different failure modes. Electro-galvanized steel specimens without silane treatment showed an adhesive failure. However, silanized specimens exhibited predominantly cohesive failure.

#### **4. CONCLUSION**

In this work the effect of the ethanol/water ratio on the hydrolysis time for a 1% bis-sulfur silane solution at pH 6 was studied. FTIR spectroscopy was used to determine the best ethanol/water ratio. In addition, mechanical test and corrosion test were carried out to evaluate the behaviour at different hydrolysis times and pH values for the optimal ethanol/water ratio.

The FTIR-ATR technique allows a good monitoring of the hydrolysis process of bis-silane dilute solutions. It is clear that increasing the ratio of ethanol/water causes the peaks of the ethoxy groups to decrease faster.

The FTIR-RA technique allows a good study of silane surfaces obtained from dilute solutions.

The shear test shows that the use of DS + MPS coatings applied by means of the two-step process leads to increased adhesive strength. Therefore, silanization can be concluded to favour bonding between the adhesive and galvanized metal. The highest adhesion results are obtained for the DS solution at pH 6. Increased hydrolysis time of the silane solution leads to reduced adhesive strength at pH 6 and increased adhesive strength at pH 4.

Finally, the importance of silane thickness on adhesion and corrosion resistance is also observed.

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