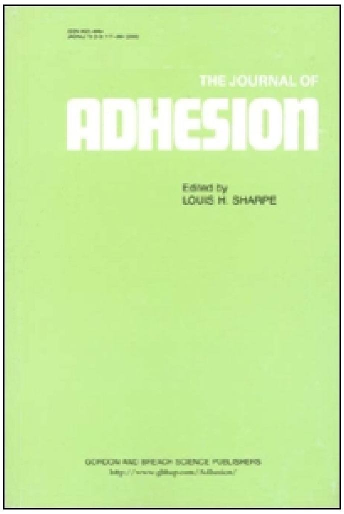

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Silanization of Stainless Steel Surfaces: Influence of Application Parameters*

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The adsorption of γ-aminopropyltriethoxysilane (γ-APS) onto stainless steel substrates has been investigated by Low-Energy Electron Induced X-ray Spectrometry (LEEIXS). Results reported in this work show the influence, on the film thickness, on the one hand, of silane concentration, pH, aging time and alcohol/water ratio of the γ-APS solution, and on the other hand, the influence of the drying conditions of the silane films. Clearly, these demonstrate the capabilities of LEEIXS for quantifying the amount of γ-APS adsorbed on the metallic surfaces from the silane solutions. Some correlations are also shown between spectrometric results and mechanical data (practical adhesion measurements) provided by a three-point flexure test.

KEY WORDS: silane coupling agents; adhesion promoters; stainless steel surfaces; epoxy adhesives; bonded joints; surface analysis; low-energy electron induced x-ray spectrometry (LEEIXS); practical adhesion measurements; three point flexure test; silanization mechanisms.

INTRODUCTION

Silanes are commonly used as coupling agents[1,2] to enhance adhesion between polymeric and inorganic materials, *e.g.*, between glass fiber surface and matrix in a reinforced plastic composite or between polymer coating and mineral substrate (glass, ceramic, metal). In order to understand the mechanisms of silane adsorption onto solid surfaces, extensive efforts have been made in the last decade to characterize the chemistry of the coupling agent/substrate interface and of the silane interphase itself when silanes containing different functional groups are used.[3–5] Let us recall here that silane coupling agents have generally the structure $R'—Si—X_3$ where X is a hydrolyzable (generally alkoxy) group capable of reacting with the substrate and R′ a reactive group selected for bonding to the polymer adhesive. In aqueous solutions, hydrolysis occurs stepwise to form alkoxysilanols and probably also silane triols (Fig. 1a). The so-formed silanol groups are extremely reactive and condensation reactions proceed readily either with other alkoxysilanols (condensation mechanisms: Fig. 1b) or with silanols present on the mineral substrate

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(silanization mechanisms: Fig. 1c). This silanization process is reported to occur mainly by hydrogen bonding when the silane solution enters into contact with the substrate and by further covalent M—O—Si oxane bond formation when silane films are dried.[1,2] However, there also exists some evidence (^{1}H-^{29}Si CP-MAS NMR experiments) that silanization agents (methylchlorosilanes and methyltrimethoxysilane) in aqueous solutions can also react (*via* silanol groups) directly with solid surfaces and form chemical bonds (oxane bonds) with these surfaces.[6,7] As shown by various studies, the chemical stability of the oxane bonds is largely dependent on the nature of the mineral substrate.[8] Reactions depicted in Figure 1 proceed at rates which change as a function of various parameters such as the organofunctionality (nature of the R′ group), organic solvent-water mixture, concentration of silane, pH, temperature and aging time of the solution. Under these conditions, improving the quality of the silane/substrate interface requires optimization of the silanization process by enhancing the hydrolysis step and minimizing the condensation step. During the last decade, many insights on this subject have been gained by using modern spectrometric techniques such as XPS[3,9], SIMS[10,11], FTIR[3,12,13] and NMR.[14] In this work, we discuss:

- firstly, the deposition of thin γ-aminopropyltriethoxysilane (γ-APS) films on stainless steel substrates. It is worth recalling here that the surfaces of reactive metals must often be covered for specific applications with polymer coatings and that an organosilane film may be intentionally formed as a transition zone (interphase) between coating and substrate to ensure one or more specific properties. For example, such a transition zone may be developed in order to create strong chemical bonds at the coating/substrate interface which allows both improving the protection of the corresponding system against any chemical or electrochemical attack by agressive species and making such a system more resistant to any mechanical stress.
- secondly, how to get a better understanding of the influence of experimental parameters (γ-APS concentration, solvent/water ratio, pH, age of the silanization agent solution, and drying temperature of the silane film) on the kinetics of the hydrolysis and condensation reactions on the one hand, and on the structure and adhesion-promoting properties of the so-formed interphase on the other hand.
- thirdly, the capabilities of Low-Energy Electron Induced X-ray Spectrometry (LEEIXS)[15-18] for analyzing very thin insulating organic films and quantifying the silane amounts deposited on the metallic substrate as a function of the parameters cited above.

EXPERIMENTAL

γ-APS was obtained from Hüls-Petrach. Silane solutions (up to 1.2%) were prepared with a mixture of distilled water and ethanol. The natural pH of these solutions is 10.6. In a series of experiments adjustment of the pH from 10.6 to lower values was

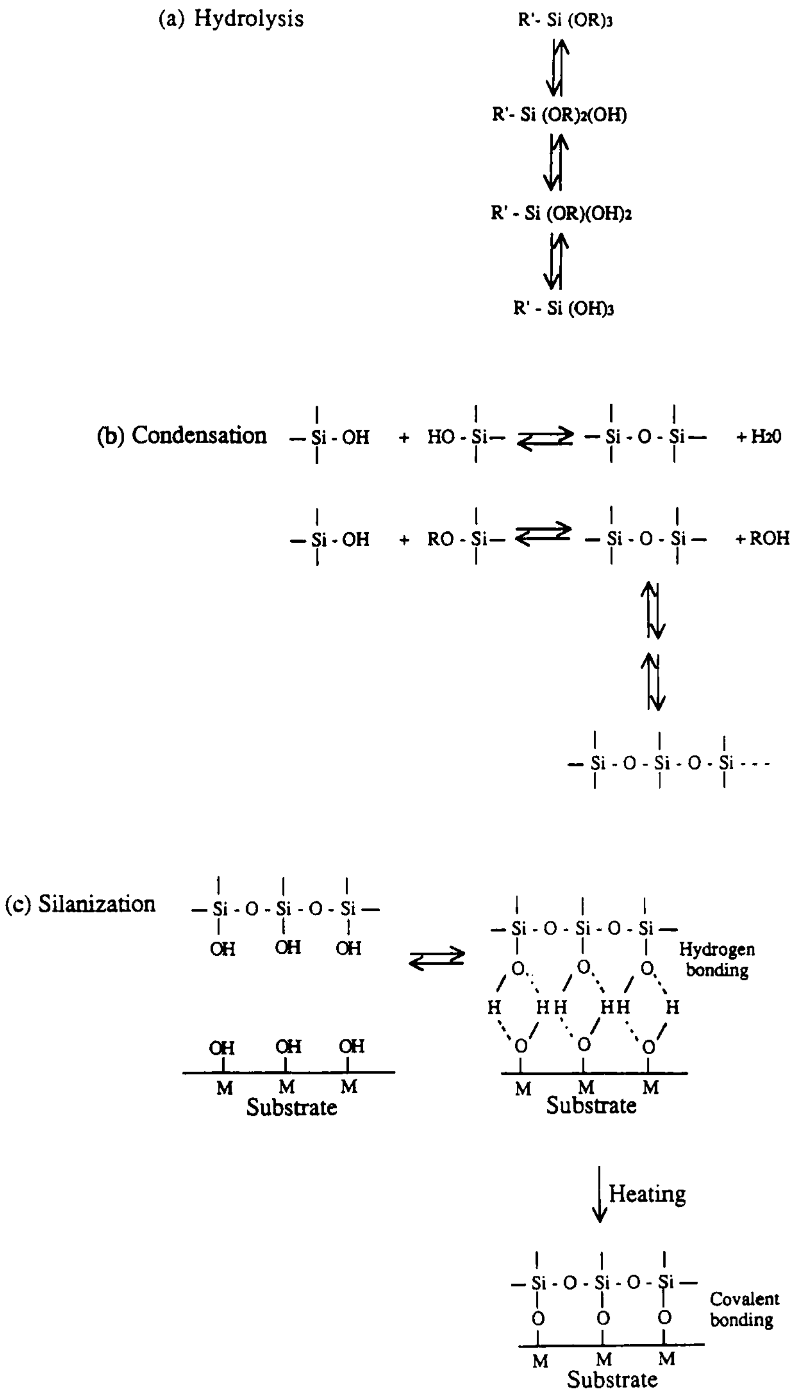

FIGURE 1 Reactions and bonding mechanisms of alkoxysilanes.

obtained using acetic acid. The substrates used were 1 mm thick AISI 304 L stainless steel panels manufactured by Ugine-Gueugnon, France, supplied in the bright anneal state and all die-cut to 1 × 5 cm coupons. Prior to silane deposition, the coupons were cleaned ultrasonically in acetone at RT for 5 min then dipped in acetone at 60°C for 5 min, chemically treated in a sulfochromic bath at 60°C for 10 min, rinsed with distilled water and blown dry with nitrogen. After cleaning and pretreatment, all substrates were then subjected to silanization by dipping in solutions 1 min after preparation of the latter. In all cases, dipping duration was 1 min. In such experimental conditions, the solution remains mainly constituted with silane monomers partially and/or entirely hydrolyzed and not at all with oligomers resulting from condensation reactions. Such facts were confirmed for a 1% γ-APS solution by ^{29}Si NMR experiments (not described in this work). The silane films were blown dry with nitrogen and heated for 1 hour at 100°C in air. After this step, the silane films were rinsed in distilled water for 2 min in order to remove any weakly bound or physisorbed species. The specimens for the adhesion test were then obtained by bonding with an epoxy adhesive (3M 3525 B/A) which was cured for 2 hours at 80°C. These specimens were maintained at room temperature for 24 hours before testing.

The LEEIXS instrument (Fig. 2) is basically a wavelength-dispersive X-ray spectrometer in which the excitation tube is an electronically-stabilized gas-discharge source. Such a system operates as an electron source under the primary vacuum of the spectrometer. The quasi-monokinetic electron beam generated is not focused on the sample surface and the area analyzed is less than 1 cm^2. The latter depends on the choice of the size of the hole in the anode which allows a part of the electron beam to escape from the discharge tube and to reach the specimen under investigation. Typical operating conditions are in the 1–5 kV range with a current between 0.1 and 0.5 mA. Soft and ultrasoft X-rays emitted in such conditions are dispersed as

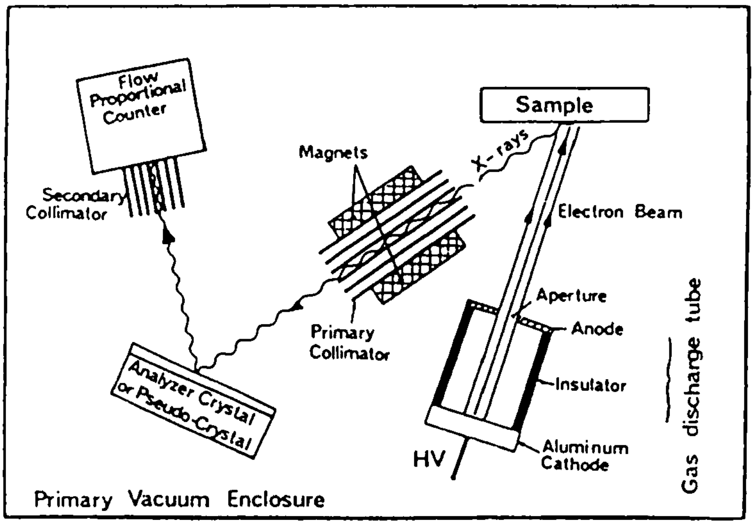

FIGURE 2 Schematic diagram of the LEEIXS spectrometer.

a function of their wavelength by suitable flat analyzing crystals, pseudo-crystals or synthetic multilayers and detected by a flow-proportional detector equipped with a thin aluminized polypropylene window (0.5 μm) and swept with a conventional 90% Ar-10% CH_4 gas mixture. The depth probed depends, among other parameters, on the incident electron beam energy and on the chemical nature of the sample and typically ranges from 5 to 100 nm. This technique allows both atomic (qualitative and quantitative) and molecular (qualitative) analysis. It should be noted that LEEIXS is particularly well suited to light element detection (B, C, N, O, F, ⋯ from their K_α radiations) owing to a high ionization cross-section of the K shells by low-energy electrons and a relatively high current of the incident electron beam penetrating in a relatively large sample volume ($\sim 10^{-12}$ cm^3). In addition, it should also be said that LEEIXS, account being taken of the nature of the excitation source used, allows the analysis of insulating samples without the need to cover them with a conducting film, and that the current density of the electron beam at the sample surface is normally chosen low enough (*e. g.*, 0.1 mA. cm^{-2}) to prevent the degradation of many materials and more particularly of various organic ones.[18]

In addition, some experiments were carried out by XPS. The spectrometer used is a part of a Riber SIA 200 surface analysis system[21] equipped with a twin anode (Mg and Al) nonmonochromatized x-ray source and a MAC 2 analyzer. All scans given in this work were obtained with the Mg source and recorded at overall resolution of 2.3 eV and at a detection angle of 65° between analyzer and sample surface. Binding energies were referenced to the C1s signal at 285 eV representative of C—C and C—H bonds.

Adhesion measurements were carried out using a three-point flexure test (AFNOR norm: NFT 30010) and a tensile machine (Flex 3 from Techmetal, France). A set of 6 joined assemblies was prepared for each series in order to obtain statistical reproducibility. The specimen geometry has previously been described.[19,21] A computer-controlled system was used to monitor the cross-head displacement (0.5 mm.min^{-1}), record the "load/displacement" curve in real time and calculate the parameters of interest. In this work, ultimate displacement (d_{max}) for obtaining the specimen failure was selected to characterize the practical adhesion. In each figure showing adhesion data, results for each series are represented by a rectangle whose height indicates the statistical error and whose central point indicates the average value.

RESULTS AND DISCUSSION

Influence of the γ-APS Concentration

Figure 3 provides LEEIXS results and shows CK_α, OK_α and SiK_α band or line intensity variations as a function of γ-APS concentration of the solution. For this study, the ethanol/water ratio is taken equal to 25/75 by volume. As can be seen the silane film thickness (to a first approximation, proportional to the SiK_α intensity) increases up to about 0.3% of γ-APS and then decreases. This experimental observation can be explained by the fact that, for the same immersion duration (1 min) and for low γ-APS concentrations, the silane film deposited has grown in an ordered way onto the substrate surface, many hydroxyl groups originating from hydrolysis of ethoxy groups having had the possibility of reacting with sites available at the material surface. On the other hand, when the γ-APS concentration is higher than about 0.3%, defect formation and perturbation of the organisation of the silane film occurs.[22,23] Under these conditions, these less-strongly bounded structures can be easily eliminated during the water washing sequence.

As can also be observed in Figure 3, the silicon and carbon signal intensities (and therefore the Si and C content on the surface) do not follow the same trend. Initially, SiK_α and CK_α intensities both increase as the thickness of the silane film increases. Then, the SiK_α intensity decreases while the CK_α intensity remains practically constant. A possible explanation of this last experimental result is that the CK_α intensity is due to several complex origins (C in the substrate, C from the pre-existing superficial contaminants, C from the polysiloxane film itself and possibly C from reaction products between the aminated silane and carbon dioxide[24] and from hydrolysis products between the solvent and the polysiloxane film). Lastly, it should be noted that for ultra-thin silane films, such as those considered in this work, NK_α radiation intensities were not measured. The reason for this is the low detector collection efficiency for the NK_α radiations. Indeed, these radiations at 31.6 Å are heavily absorbed by C atoms (carbon K absorption edge at 43.68 Å) contained in the polypropylene thin film constituting the window of the flow proportional counter. Under these conditions, the LEEIXS investigation of the N/Si concentration ratio of very thin silane films was not carried out to compare with Domingue *et al.*'s results[25] which suggest a loss of nitrogen atoms from such films and their degradation when dried in contact with crystalline Si substrates. Indeed, these authors have proposed a mechanism which involves the reaction of the amine moieties with the substrate surface *via* the coordination of nitrogen atoms with metal ions and the subsequent homolytic scission of N—C bonds. However, it should be said that such a mechanism, insofar as it has to be verified, is certainly strongly dependent

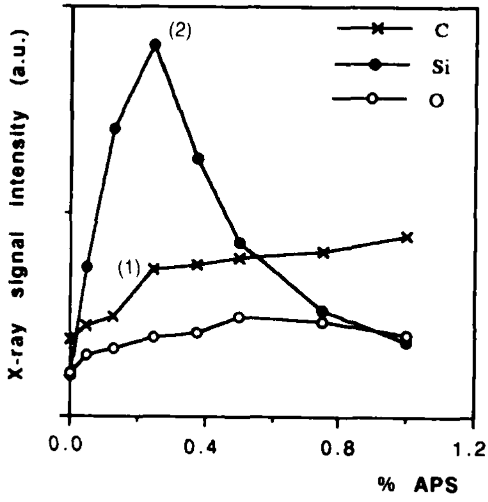

FIGURE 3 Effect of the γ-APS concentration in the silanization solution on the thickness of the silane film deposited (SiK_α intensity measured by LEEIXS is proportional to the thickness).

upon the electronic properties of the substrate surface, *i.e.*, of the nature of the substrate after treatment.

In order to confirm the LEEIXS results, XPS analyses were also carried out. Figure 4 represents survey spectra recorded from the stainless steel surface after the chemical treatment, and from the same surface covered either with thin silane films (whose thicknesses correspond to points marked (1) and (2) on the curve of Figure 3) or with a thicker film which was not submitted to the last washing sequence (see Fig. 15). Because of the very low ionization cross-section of SiL shells the intensity of the Si2p photopeaks is quite weak and the corresponding signals are hardly visible. On the contrary, the presence of the silane layer is highlighted by the decreasing of the substrate signal (Cr2p and Fe2p photopeaks) intensity. As long as the latter does not disappear completely the thickness of the silane layer remaining after the washing sequence can be estimated at about a few nanometers under the hypothesis

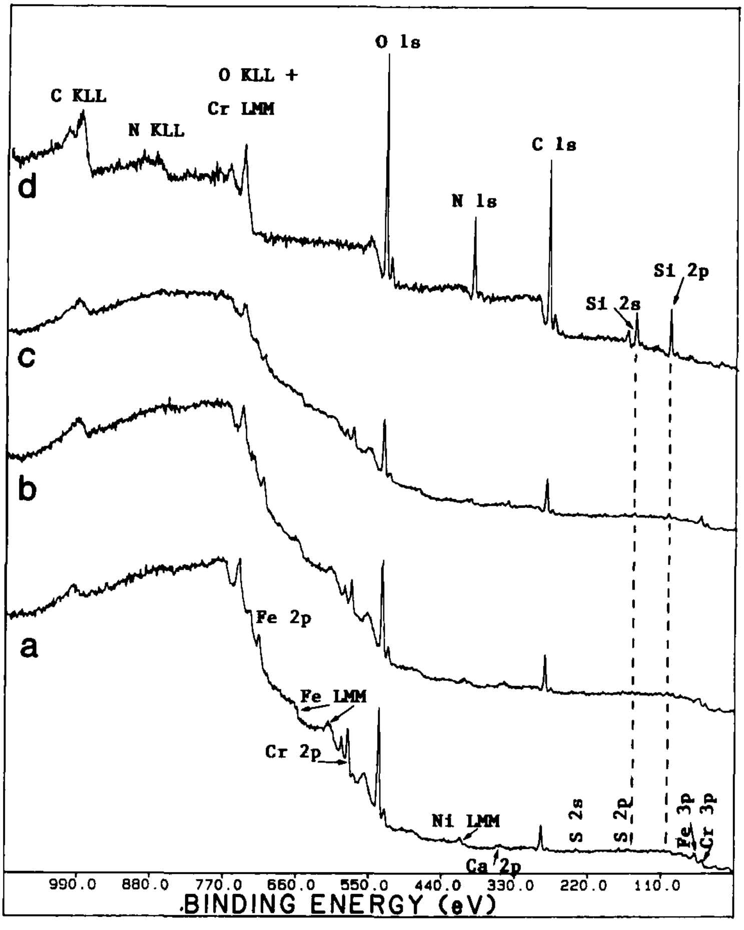

FIGURE 4 XPS survey spectra of stainless steel surfaces: (a) chemically treated, (b) and (c) covered with a thin γ-APS layer, and (d) covered with a thick and unwashed γ-APS layer.

of a uniform layer. In addition, Figure 5 shows a comparison of the XPS Si2p spectra from the same samples as in Figure 4. The Si2p spectrum (a) of the reference sample (chemically-treated specimen) at a binding energy of 101 eV is mainly due to the contribution of silicon present in the steel, in its elemental state and in its oxidized state at the uppermost surface. On the contrary, the photopeak observed at 102.3 eV (spectrum *d*) is characteristic of only the silane layer. The corresponding chemical shift (1.3 eV) agrees with the fact that Si atoms from γ-APS are linked both with O atoms and with C atoms from aliphatic chains. Obviously (b) and (c) intermediate Si2p spectra at about 101.9 eV are both due to the contribution from the substrate and from a thin silane layer. Owing to the low intensity of these Si2p photopeaks they were not deconvoluted in their components.

In the same way, Figure 6 represents the changes in adhesion properties of adhesive/silane film/metallic panel systems as a function of γ-APS concentration. The highest bond strength was obtained for about 0.12% of γ-APS. This value confirms numerous literature data[1,2,23] and is in agreement with the fact that solutions containing low concentrations of γ-APS are mainly made up of reactive monomeric silanols. It should also be noted that this value corresponds to the optimal thickness of the coupling agent film which presents many strong bonds at the silane/film substrate interface and an appropriate network allowing an interpenetration with the adhesive. Indeed, let us recall that literature data generally report the existence of a particular concentration of the γ-APS solution (at about 0.15%) below which there is a quasi-perfect organization of the monomeric molecules onto the substrate surface and above which less-strongly organized monomeric structures are formed and partly eliminated by the washing sequence.

Finally, it should be said that some works reported in the literature also give higher values of the γ-APS concentration for which a maximum joint strength can

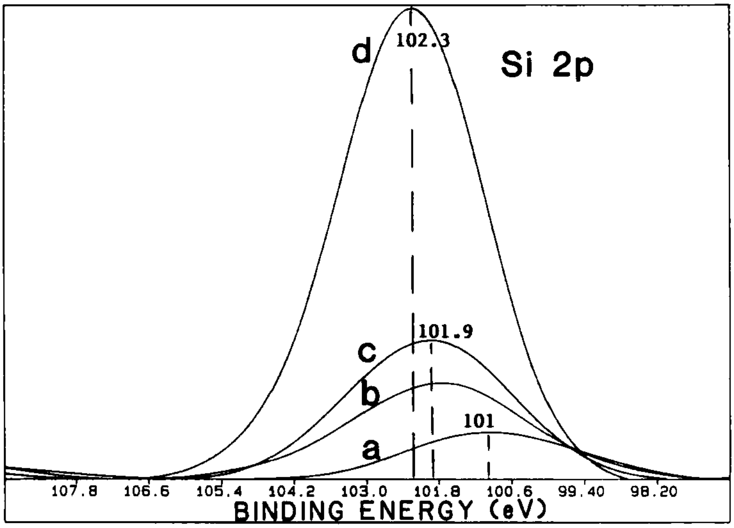

FIGURE 5 Si2p XPS spectra of stainless steel surface: (a) chemically treated, (b) and (c) covered with a thin γ-APS layer, and (d) covered with a thick and unwashed γ-APS layer.

be observed. By way of example, Sung *et al.*[26] show a 180° peel strength maximum of a α-Al_2O_3/γ-APS/polyethylene joint for a γ-APS concentration of about 2%. However, such results cannot be compared with those obtained in the present investigation, even though the general shape of the experimental curve is quite similiar, because of the different natures of both the substrates (α-Al_2O_3) and adhesive (thermoplastic polymer) used and because of the different interactions occuring, particularly between the adhesive and silane film (purely interdiffusional interactions).

Influence of the Ethanol/Water Ratio

As reported in the literature, the role of alcohol in aqueous solutions of silanes is to avoid and delay the formation of large and highly-oligopolymerized aggregates.[23] Figure 7 shows the changes in adhesion properties of the adhesive/silane film/metallic panel systems when the ethanol/water ratio changes. In these experiments, the γ-APS concentration is kept equal to 0.12%. The highest bond strength was obtained for a ratio of about 75/25. It should be noted that no precise indications are reported in the literature about the influence of this parameter, various ratios being commonly used and in particular the 25/75 ratio which is considered in the remainder of this study. LEEIXS experiments in this field also demonstrate that silane film thicknesses do not change significantly.

Influence of the γ-APS Solution Aging

Figures 8 and 9 represent on the one hand, CK_α, OK_α, SiK_α intensity variations, and on the other, adhesion property changes as a function of the solution aging after

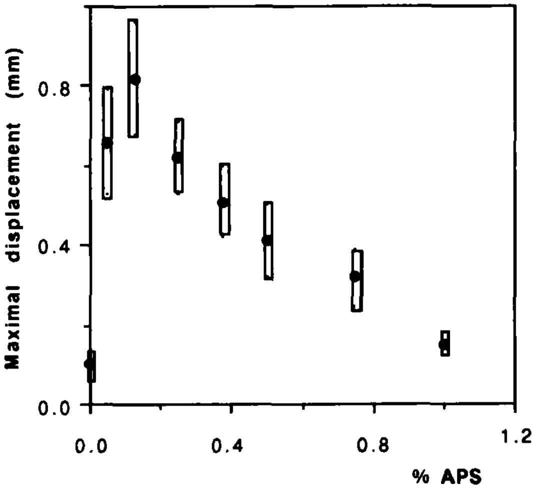

FIGURE 6 Effect of the γ-APS concentration on the bond strength of epoxy adhesive/silane layer/metallic substrate joints (EA/SL/MS joints).

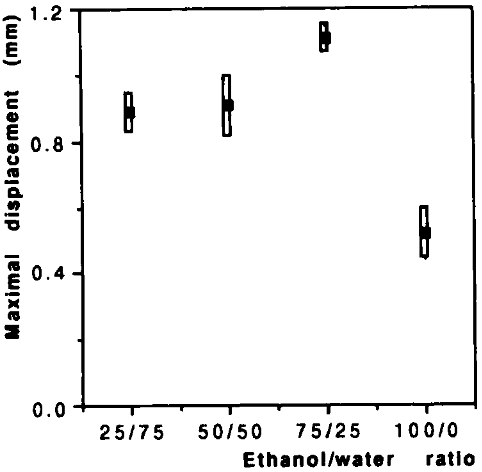

FIGURE 7 Effect of the ethanol/water ratio on the bond strength of EA/SL/MS joints.

preparation of the initial mixture. In these experiments, the γ-APS concentration and the dipping duration are taken equal to 0.12% and 1 min, respectively. As can be seen, the silane film thickness increases up to 800 seconds of aging. Over this duration, the condensation reactions taking place in the solution are always partial and under these conditions the solution remains essentially constituted of stable monomeric silanols which are prone to react easily with sites available at the material surface. For longer aging times, condensation reactions are little more advanced and badly-ordered structures are produced which are, here again, partially eliminated by the washing sequence. In other words, there is a concordance between this situation and that occuring when high γ-APS concentrations and 1 min aging time are used (see Fig. 3). In addition, it is worthy of note that the initial decreasing of the CK_α signal intensity is associated with the hydrolysis reactions which progressively replace ethoxy by hydroxyl groups. Further increasing of this same signal follows the SiK_α intensity variations, *i.e.*, the changes in silane film thickness. Concerning now Figure 9, and adhesion properties of the corresponding silane layers, it should be noted that the influence of film thickness is similar to that already described (see section on "Influence of the γ-APS concentration").

Influence of the Solution pH

Usually, pH is a parameter frequently taken into account to keep under control the silanization process.[27] Both hydrolysis and condensation kinetics are pH-dependent. For instance, Pohl[28] shows that the slowest rate of hydrolysis of γ-substituted coupling agents (γ-APS, γ-MPS and γ-GPS) is at about pH 7 while the slowest rate of condensation should be at around pH 4. As a general trend, the silanization process would be favored by acidic solutions in which hydrolysis is maintained fast while

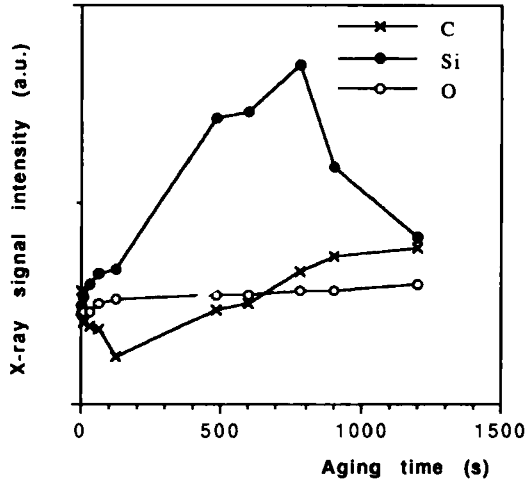

FIGURE 8 Effect of the γ-APS solution aging on the thickness of the silane film deposited (LEEIXS measurements).

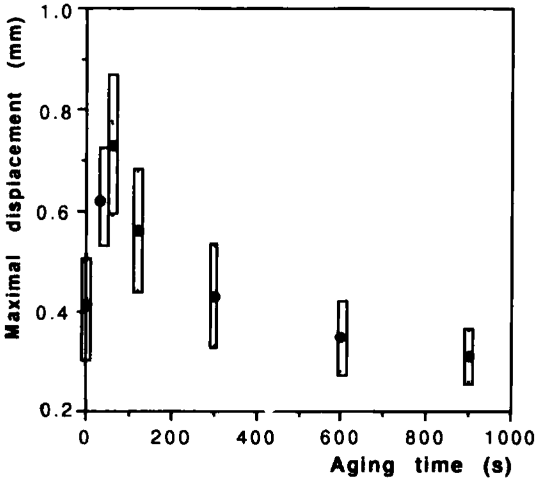

FIGURE 9 Effect of the γ-APS solution aging on the bond strength of ES/SL/MS joints.

condensation is kept slow. However, in the particular case of γ-APS, the silane solution is generally employed at its natural pH (10.6). Indeed, it is known that at alkaline pH the hydrolysis of γ-APS leads to the formation of hydroxysilanes which are stabilized in solution by hydrogen bonding[29] and that this condensation delay promotes the chemical reaction of the corresponding monomers with the surface sites. Moreover, it should also be mentioned that the surface potential of a substrate varies with the pH of the applied solution which would affect the orientation of the adsorbed silane layer.[12] (Fig. 10) represents the effects of the pH variation (acetic acid addition) on the adhesion properties of adhesive/silane film/metallic substrate system. The results obtained are in good agreement with almost all the literature data[1]. Figure 11 gives LEEIXS results. As can be seen, SiK_α, OK_α and CK_α intensities do not change significantly when pH varies; silane film thicknesses behave in the same fashion. The reasons why no correlations in this particular case can be achieved between mechanical and spectrometric data are not clear at this time but they are undoubtedly associated with the complex influence of the pH changes on the film structure and on the orientation of the film towards the substrate surface.

Turning again to the influence of pH of the γ-APS solution, it should be noted that Thiedman *et al.*[29] have reported contradictory results to those obtained in this work. Indeed, these authors show that γ-APS primers are more effective when applied to aluminium substrates at pH 8, the corresponding solutions being acidified by hydrochloric acid addition. A similar trend was also reported by Boerio *et al.*[12] when HCl and an iron substrate were used. However, such an improvement was not obtained with titanium substrates for which the natural pH (10.6) of the γ-APS would be required. It is, therefore, clear that performances of γ-APS primers for adhesive/metal joints are not only governed by the molecular structure of the silane films but also by acid/base interactions which are obviously dependent upon the intrinsic properties of the substrate surfaces. In order to observe the eventual influence of the acid used for modifying the pH solution, additional experiments concerning adhesive/silane film/stainless steel systems were carried out by using hydrochloric acid instead of acetic acid. Mechanical results represented in Figure 12 show quite a similar trend and, therefore, confirm results given in Figure 10.

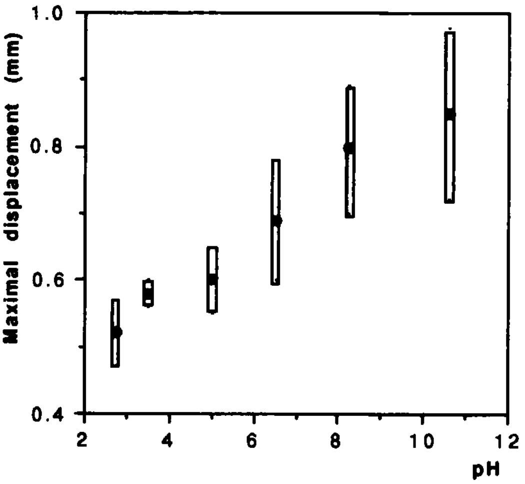

FIGURE 10 Effect of the pH of the γ-APS solution (acetic acid addition) on the bond strength of EA/SL/MS joints.

Influence of the Film Drying Temperature

Figure 13 shows the influence of the drying temperature of the silane film on the adhesion properties of the whole system. Best performances are obtained between 100 and 150°C. Above this range, interdiffusion of silane and epoxy adhesive is lower[30]. Indeed, the high temperature is responsible for a much more significant condensation

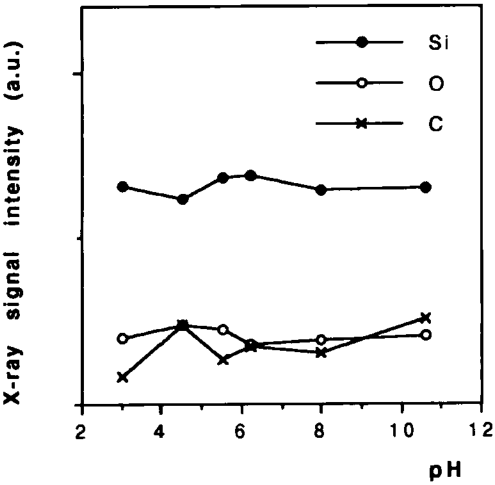

FIGURE 11 Effect of the pH of the γ-APS solution on the thickness of the silane film deposited (LEEIXS measurements).

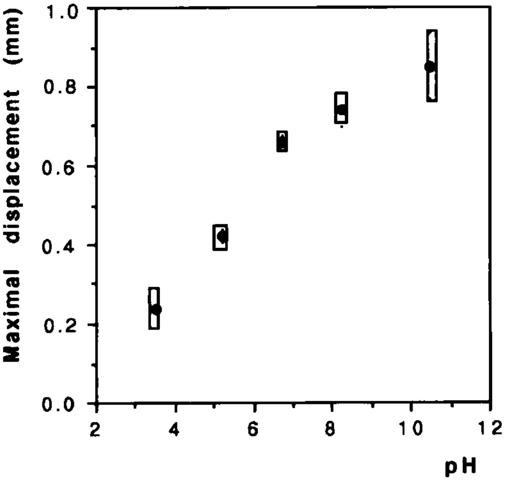

FIGURE 12 Effect of the pH of the γ-APS solution (hydrochloric acid addition) on the bond strength of EA/SL/MS joints.

of the remaining silanol groups and, consequently, for the formation of a dense silane network which limits the respective mobilities of silane and adhesive.

Influence of the Washing Time of the Dried Film

Figure 14 shows results obtained by LEEIXS, namely the decreasing of the SiK_α intensity as a function of the washing time in distilled water. These experiments were carried out with silane films which were dried at 100°C for 1 h in air. As can be seen,

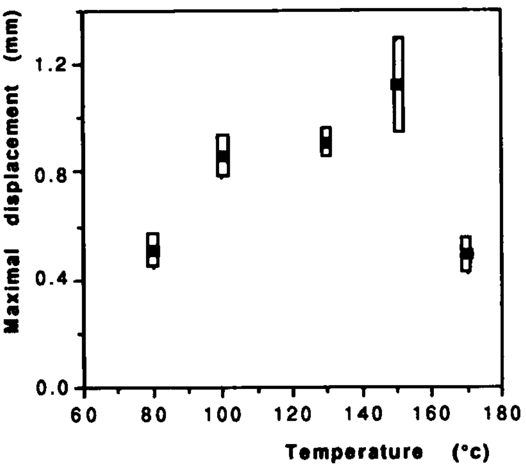

FIGURE 13 Effect of silane film drying temperature on the bond strength of EA/SL/MS joints.

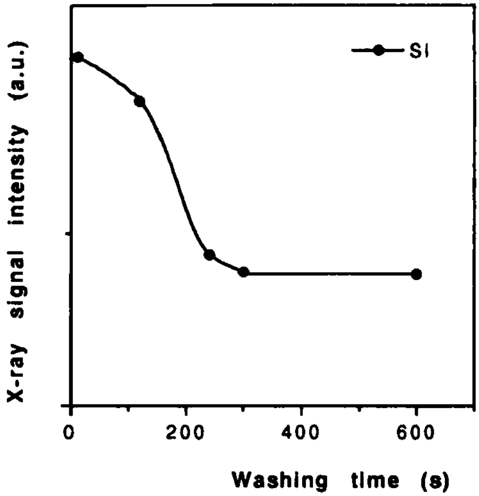

FIGURE 14 Effect of the washing time on the thickness of the dried silane film (LEEIXS measurements).

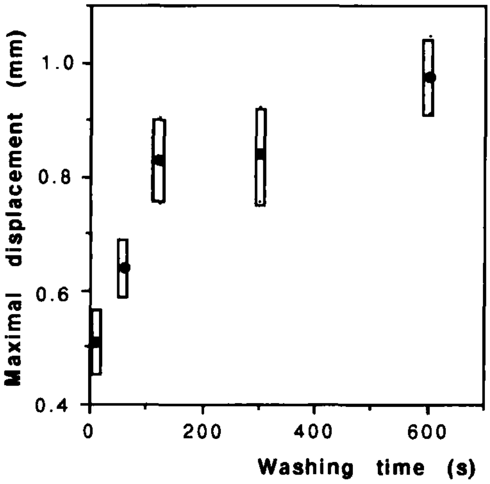

FIGURE 15 Effect of the washing time of the dried silane film on the bond strength of EA/SL/MS joints.

2 min are necessary for removing the main part of the weakly bound or physisorbed species. This duration justifies the choice made in all the previous experiments. Figure 15 shows adhesion measurements which are in good agreement with such an explanation.

CONCLUSIONS

In dealing with these silane deposits we clearly demonstrate the capabilities of the LEEIXS method for analysing thin insulating organic films deposited on metallic substrates. The original approach undertaken in this study permits a better understanding of the influence of various experimental parameters on the kinetics of the hydrolysis and condensation reactions and on the formation of the silane layers, and confirms some results reported in the literature. Further studies using, in particular, XPS and FTIR techniques are in progress to obtain complementary data.

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