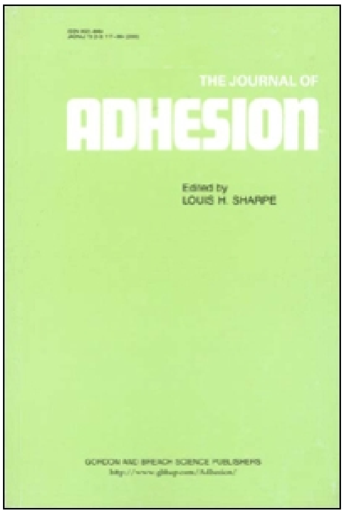

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THE INFLUENCE OF PROCESS PARAMETERS ON THE INTERFACIAL CHEMISTRY OF γ-GPS ON ALUMINIUM: A REVIEW

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THE INFLUENCE OF PROCESS PARAMETERS ON THE INTERFACIAL CHEMISTRY OF γ-GPS ON ALUMINIUM: A REVIEW

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Within the "International Collaborative Programme on Organosilane Adhesion Promoters" (ICOSAP), scientists from the U.S. and Europe contributed to the understanding of an organosilane primer process, based on an aqueous solution of γ-glycidoxypropyl trimethoxysilane (γ-GPS), used currently for aerospace repair purposes. Parameters such as temperature of cure, ageing time, and concentration of the aqueous solution have been investigated, and this work reviews the effect that each variable has on the process, and the resulting integrity of the GPS/aluminium interface. The aim of the work was to provide a more environmentally friendly replacement for pretreatments containing Cr(VI) that are currently used, such as chromic acid anodising and acid etching employed for the structural adhesive bonding of aluminium.

The formation of covalent interfacial bonding is shown to be a function of the hydrolysis and condensation of the silane molecules in solution as well as the type of solvent used. The curing temperature of the aqueous film on the aluminium is also

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shown to have an effect on the chemistry of the resulting primer film and its efficacy as an adhesion promoter. All these parameters must be optimised to obtain durability that matches that obtained by a phosphoric acid anodising pretreatment. This work reports on the various studies performed towards this aim carried out within the remit of the ICOSAP initiative, with a particular emphasis on the interfacial chemistry between γ-GPS and the aluminium substrate, and indicates the manner in which the results point the way towards a viable, environmentally friendly pretreatment for the adhesive bonding of aluminium for aerospace applications.

Keywords: Organosilane; Aluminium; Hydrolysis; Durability; XPS; ToF-SIMS

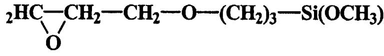
INTRODUCTION

Organosilanes are good candidates for the replacement of chromium (VI)-based pretreatments for aluminium as well as in various other applications where improvement of interfacial interactions is required to increase the lifetime of a finished product, *i.e.*, the durability of an adhesive bond or organic coating on a metallic substrate. They are relatively innocuous to the environment as only the residual alcohol produced during the hydrolysis may be harmful (only strictly true for methanol) and they may be used either as a primer or within an adhesive or organic coating formulation. It is widely accepted that, when applied to a metallic substrate, a covalent bond is produced *via* condensation of the silanols of the hydrolysed silane and hydroxyl functionalities present at the metallic oxide surface. However, there is little direct evidence of this bond in the literature. The principal inconvenience when using silanes is that their chemistry may be influenced by relatively subtle changes in a wide range of parameters, such as temperature, moisture, type of solvent or mixture of solvents, mode of application, and ageing time of the solution. Thus, although there is a large body of literature (both academic and commercial) on the methods of use and mode of action of organosilanes, such experiments have been carried out in a piecemeal fashion with, in some cases, relatively poorly defined process parameters. The work described in this review was an attempt to rectify this shortcoming by carrying out a series of controlled experiments, across three continents, to establish the structure/property relationships relating to silane on a single substrate.

This programme, the "International Collaborative Programme on Organosilane Adhesion Promoters" (ICOSAP), has been described in some detail by Digby and Shaw [1], the coordinator and originator of the project, respectively. In brief, it involved scientists from the UK, U.S., France, Canada, and Australia, all funded through their usual national channels but working on a common theme. The University of

Surrey's role was to study the effect of selected parameters in order to establish how they affected the interaction of a silane film with the aluminium substrate (2024-T3). The starting point for this work was the recommendations of Kuhbander and Mazza [2], from the Wright Patterson Air Force Base Laboratories, which were as follows: 1% GPS aqueous solution (pH 5) left to hydrolyse for 1 h, brushed onto grit-blasted (50 μm fresh alumina grit) 2024-T3 aluminium alloy for 10 min and dried at 93°C for 1 h [2]. This set of parameters was known to give a surface pretreatment that yielded adhesive joints of good durability, and even at the start of the programme (in 1996) test examples had been flying for some considerable time. Wedge cleavage tests (Boeing wedge tests) were performed by various partners within the programme to assess bond durability and also to provide a round robin exercise to ensure that similar results were obtained by different operatives in different countries. The durability data from these tests were reported as a function of the various parameters studied. To study, at a fundamental level, the effect of process parameters such as concentration of silane solution, temperature of drying, ageing time, and solvent type a simple system was chosen: an alloy that does not contain any silicon, a film of hydrolysed silane coating the alloy surface, and an epoxy adhesive that does not contain any silane. For convenience, the University of Surrey work was carried out using commercially pure aluminium (99.9%) and MilliQ water at natural pH (~6).

The organosilane used was γ-glycidoxypropyl trimethoxysilane (γ-GPS), the structure of which is presented below:



$$\underbrace{{}_2HC-CH}_{O}-CH_2-CH_2-O-(CH_2)_3-Si(OCH_3)_3$$

The 1% aqueous solution of this silane was adsorbed or coated onto either a clean aluminium surface or on grit-blasted aluminium to replicate the process used in the field and recommended by Kuhbander and Mazza.

COVALENT BOND FORMATION BETWEEN METALS AND SILANES

The formation of a covalent bond between oxidised metal surfaces and organosilanes has long been postulated and, indeed, proven indirectly *via* the improvement of joint strength and hydrolytic stability [3]. However, organosilane molecules are not often used in an optimum fashion to ensure the maximum improvement of the durability of the metal/polymer interface. For this reason, it is also important to be able to establish analytically, *i.e.*, directly rather than indirectly, that covalent bonds are formed between the molecules and the substrate of choice. Direct evidence of this reaction is lacking in the literature on the subject and, consequently, this section describes experimental work reporting on γ-GPS and other silanes.

Detection with Surface Mass Spectrometry

One of our main interests within the ICOSAP programme was to establish unambiguously the evidence of covalent bond formation between GPS and aluminium. In the past, other authors have claimed the presence of an $\mathrm{Al\text{-}O\text{-}Si}^+$ fragment in the secondary ion mass spectrum (SIMS) of aluminium treated with GPS. Fang *et al*. reported the formation of covalent bonds between GPS and aluminium through the use of SIMS [4]; however, the spectrum for which they claimed that an ion at $m/z = 71$ may be assigned to $\mathrm{Al\text{-}O\text{-}Si}^+$ is from an aluminium substrate coated with a layer of GPS that will not allow for detection of an ion arising from an interfacial interaction, using a surface-specific method such as SIMS. This is confirmed by examining the low mass region of the spectrum as the intensity of the ion at mass $m/z = 27$ is similar to that of $m/z = 29$. This is a very well-known method used in ToF-SIMS to assess the amount of organic material present on an aluminium surface and, in this particular case, indicates that the ions presented in this spectrum are arising from an organic film rather than from the interface silane/aluminium (*i.e.*, no aluminium contribution towards $m/z = 27$, which would not produce an intense signal at $m/z = 29$ and, therefore, no detection of interfacial ions can be achieved from this specimen). Moreover, the assignment of fragments at $m/z = 71$ is not necessarily a simple process as there are as many as six or seven fragment ions within the mass range of $m/z = 70.9$ to 71.15 for an aluminium sample treated with GPS, as we will illustrate below. Thus, the work of Fang *et al*., which was carried out using a quadrupole system with a nominal mass resolution of unity, can be discarded on two counts, a thick film and insufficient spectral resolution of their SIMS system. Abel *et al*. studied the interaction of GPS on the surface of grit-blasted aluminium [5, 6]. The hydrolysed solution of 1% γ-GPS was brushed as recommended on the grit-blasted surface of pure aluminium for only 2 min to form a thinner film than for the industrial process and allow for analysis of the interfacial bonds. To demonstrate that covalent bonding occurs, the fragment $\mathrm{Al\text{-}O\text{-}Si}^+$ has to be present within the region of nominal mass $m/z = 71$, and to establish this unequivocally a time-of-flight analyser is required (*i.e.*, ToF-SIMS). An example of high mass resolution spectrum of this region, recorded on a ToF-SIMS system, is

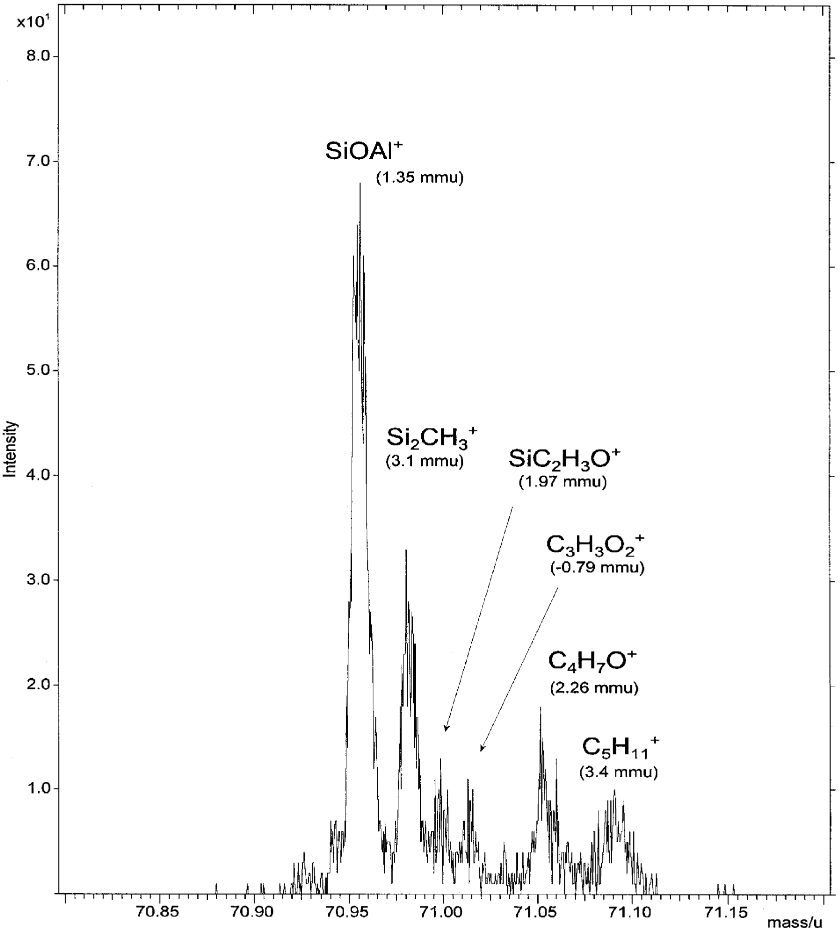


FIGURE 1 High resolution mass spectrum of γ-GPS–coated aluminium in the mass range of $m/z = 70.9$ to 71.15 Daltons (figure in parentheses indicates the deviation, in milli mass units, from the theoretical mass).

shown in Figure 1 in which six fragments are present, the possibility of detecting Al_2OH^+ ($m/z = 70.9695$) through the silane film having been eliminated. The fragment Al-O-Si^+ is obvious in the spectrum and is sufficient to establish that interfacial covalent bonding exists. This was also accompanied by indirect evidence such as improved strength of wedge joints, then prepared with a 10 min brushing time compared with joints formed directly from grit-blasted surfaces, as shown in Figure 2 [1, 7]. Tests results obtained from double cantilever

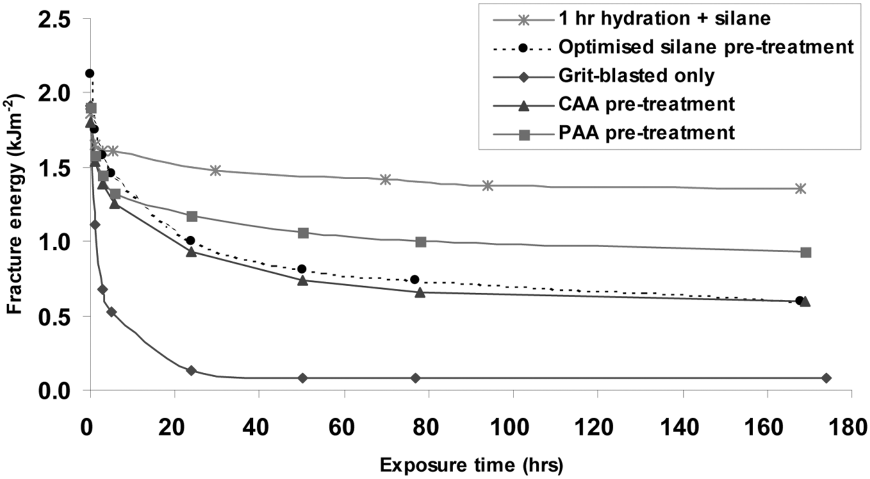


FIGURE 2 Fracture energy variation as a function of surface pretreatment of 2024-T3 aluminium alloy [7].

beam joints also exhibit the same trend, and it was shown by Kinloch *et al*. that the Al-O-Si$^+$ fragment is present for strong and durable joints but is not for those failing in a catastrophic manner such as joints prepared from buffered GPS solutions [8]. More recent work presented by Bexell and Olsson showed that for an alloy of aluminium and zinc, covalent bond formation occurs between silane and aluminium but also between silane and zinc [9], thus confirming the assumption that silanes also form covalent bonds on zinc, as postulated earlier on by Williams [10]. The above experiment found its inspiration in the work by Gettings and Kinloch [11] from two and a half decades ago, as well as work performed at the University of Surrey by Davis and Watts [12]. They were able to show that GPS interacts on iron and steel by formation, as anticipated, of a covalent bond between the hydroxyls present at the surface of the metal and the silanols or methoxy group of the silane.

In Davis and Watts [12], the adsorption of γ-GPS is performed from methanolic solution. It seems likely, therefore, that the covalent bond is the result of a direct interaction *via* the alkoxy of the silane and a hydroxy functionality on the oxidised metal surface, as no hydrolysis of the silane will have occurred in solution. This will lead to the production of the corresponding alcohol as a condensation product. This is not the accepted chemistry for an organosilane, but other unpublished work from this laboratory has reinforced this hypothesis for both iron and aluminium substrates.

In the work described in Williams [10] and Gettings and Kinloch [11], SIMS was used, and the concept of an Fe-O-Si interfacial bond was supported by the observation of an ion at even mass ($m/z = 100$, 100, nominal mass for Fe-O-Si$^+$), an unusual mass for organic material ions or iron oxide ions. For this reason, they were able to assign, unambiguously, the formation of an ion at $m/z = 100$ to Fe-O-Si$^+$, even though the latter work [12] was performed on a first-generation ToF-SIMS instrument with a mass resolution rather poorer than contemporary spectrometers. The earlier work by Gettings and Kinloch compares the effect of different silane-based primer compositions on the strength of butt joints in a water environment and on the interface chemistry [11]. Various types of silanes were used, as well as various solvents and concentrations. They concluded that a covalent bond was formed only when a 1% aqueous solution of γ-GPS was used on mild steel and also that the best durability was obtained for this particular pretreatment (brush coat of mild steel with 1% aqueous solution of γ-GPS). It was also shown that for other treatments the coverage was probably incomplete. Other explanations not mentioned in this work may include the formation of weak boundary layers by adsorption of polymerised organosilane species, in the case of aqueous solutions of γ-aminopropyltriethoxy silane; the same phenomenon may occur as a result of solution concentration being too high, incomplete hydrolysis of the organosilane in methanolic solutions and competitive adsorption between the silane and an amine curing agent. Only one piece of information is missing from this work: the time used for hydrolysis of the solution. Additionally, in early work also by Gettings and Kinloch [13], evidence of the formation of covalent bonding between stainless steel and GPS was presented in the form of a quadrupole SIMS mass spectrum (presence of a fragment assigned to Cr-O-Si$^+$ in positive SIMS, of steel treated with a silane primer, at $m/z = 96$). This result was obtained for three types of stainless steels. Evidence of bonding with iron was also presented for two of these steels and an improvement in durability was obtained for all primed steels. The related article by Davis and Watts [12] showed similar results, although for this particular work the GPS was deposited from a 2% methanolic solution. However, to ensure a good interaction, the iron substrate used ($>98\%$ purity, Goodfellows, Hientington, Cambridgeshire, UK) was immersed in water for 300 s prior to silane deposition. The XPS spectra obtained following this treatment are consistent with full hydration of the surface with formation of a thin layer of FeOOH, similar to that observed on industrial mild steel [14, 15]. By the use of careful etching of a GPS film deposited on the iron substrate treated as described above, they were able to demonstrate the formation of a covalent bond between iron and GPS. It should be noted that covalent bond formation is unexpected from a methanolic solution. The influence of the substrate itself in forming bonds from alkoxy functionalities rather than from silanols that would be formed *via* adequate hydrolysis becomes undeniable. A tentative explanation may lie within the concentration of hydroxyl functionalities present at the surface because it will be different for steel and aluminium, as indicated by their differing isoelectric points [16].

Detection of Primary Bonding at the Interphase by Other Methods

One of the first definitive studies to indicate the specific interaction between organosilanes and a metallic substrate was reported by Bailey and Castle [7]. They showed that both amino and vinyl triethoxy silanes were chemisorbed on hydroxylated iron surfaces. By exposing iron coupons to a variety of solution concentrations and determining by XPS the amount of silane adsorbed at the surface, they were able to construct adsorption isotherms; the use and relevance of such an approach in adhesion science is discussed in some detail by Watts and Castle [18]. The isotherms were of the Temkin type, indicating that although chemisorption took place the heat of adsorption was proportional to the degree of coverage of the silanes on the surface. The apparent monolayer coverage for the amino silane was significantly less than for the vinyl silane. This results from the different surface conformation of the two molecules; the amino silane will lie in a horizontal orientation as a result of a weak interaction between the amino group of the silane and the iron *d* band, as well as the expected silane-to-iron interaction. The vinyl silane, on the other hand, will be oriented vertically and, thus, the aeric density of this molecule will be much greater than the APS. It is interesting to note that some two decades after this work was undertaken molecular dynamics calculations [19] predicted the same conformations!

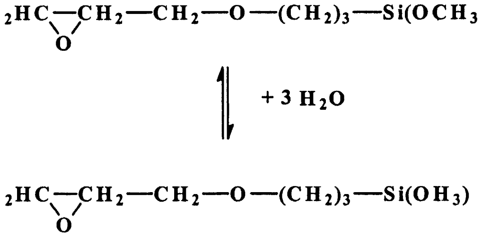
Other techniques may be used to bring evidence of the formation of covalent bonds between silanes and metal substrates. One possible method is the use of infrared spectroscopy, whereby the bond formation induces the appearance in the IR spectrum of a specific vibration band. Miller and Ishida, in their work on the interaction of silanes on lead oxide, showed the formation of a plumbosiloxane (Pb-O-Si) exhibiting an antisymmetric stretching vibration near 965 cm^{-1} [20]. In this work, the silane used was γ-methacryloxypropyltrimethoxysilane dispersed in an n-butanol or tetrahydrofuran/water solvent for which the ratio of water to silane was 10:1, and the particular technique used diffuse reflectance infrared spectroscopy. It should be noted that their assignment is in agreement with that made by Schmidbaur *et al.* for alkylplumbosilanes in the infrared vibrational region of 957 to 961 cm^{-1} [21, 22]. Similarly, Boerio and Gosselin reported a vibration near 1080 cm^{-1}, partly assigned to Si-O-Al bonds together with Si-O-Si asymmetric stretching vibration and low molecular weight oligomers, when studying the adsorption of γ-aminopropyltrimethoxysilane onto aluminium mirrors [23, 24]. The difficulty of the assignment for Si-O-Al bonds lies in the fact that silane polymerisation and silane condensation on the surface will lead to, respectively, (Si-O-Si) and (Al-O-Si) bonds of similar vibrational energy. However, the low frequency at which this band was observed leads to both conclusions that oligomers are formed and that γ-APS is strongly interacting with the aluminium surface. For this work, aluminium mirrors were treated with an aqueous solution of 1% APS, and the technique used was reflection–absorption infrared spectroscopy. These conclusions are reinforced by the work of Underhill *et al.* on the interaction of γ-GPS aqueous solutions with an aluminium alloy (7076-T6) [25]. Using principal component analysis on a series of infrared spectra, they were able to isolate two factors, capable of reporting 99% of the variance, for the region corresponding to Si-O-X bonds. It was noticed that the films examined after washing, hence with a thinner layer of γ-GPS silane on the surface, exhibited a higher proportion of factor 2 than factor 1. This factor exhibits a broad band centred at 1050 cm^{-1}, which is not present in factor 1 and, therefore, the band was assigned to Si-O-Al bonding.

A variation of the standard XPS method has been employed by Mitchell's group at the University of British Columbia to study silane interfacial chemistry. Upon the application of a negative potential bias (φ_h) to a polymer–metal interface, differential charging will ensure a variation in potential for different non-conducting regions of the sample. In XPS spectra, the structure from regions that are in direct electrical contact with the metal substrate will shift by exactly φ_h eV, but for the other regions, where an ohmic gain is experienced, the shift is f φ_h eV, where the factor f (< 1.0) depends on the local electrical characteristics. This concept was used in an attempt to demonstrate the formation of a covalent bond between silanes and aluminium when exhibiting an Al2p spectrum of which the Al^{ox} region exhibits extra structure when a bias potential is applied [26, 27]. Samples exhibiting this extra structure were either treated with GPS or γ-mercaptopropyltrimethoxysilane (γ-MGPS). Other arguments are that this effect is enhanced towards the interface; this is shown using angle-resolved XPS and is not seen on acid-etched samples before deposition of the silane. However, the conclusions reached by these authors are not convincing for several reasons. First, the XPS data indicate that heterogeneous may induce differential charging, both lateral and vertical. This is enough to induce broadening of the aluminium signal upon application of a voltage bias. Secondly, the application of the silane from a solution containing alcohol in part (50% for γ-MGPS; 95% for GPS) is not the recommended method to obtain the best possible interaction between the organosilanes and their candidate metal, as the silane will not have hydrolysed fully using such a mixture. Moreover, other scientists using very similar conditions have tested this method and no shift was noticed on the signal of the aluminium.

Another method that has potential to probe the bond formation of silane on metals is nuclear magnetic resonance spectroscopy. Anschel *et al.* demonstrated that, by using model metal materials of high surface specific area (alumina for aluminium, for example), they could amplify interface effects to bulk status [28]. Using this method and the resonance of ^{15}N nuclei, they could elucidate the chemical state of both polyimide and aminosilane (both ^{15}N enriched) at the interface with alumina. It was possible to report bond formation as well as interaction of the aminosilane *via* formation of quaternary nitrogen in aqueous solutions. It is possible to make use of the same concept for the signal of another nucleus such as ^{29}Si, of obvious interest for the study of silane interaction on various surfaces. Of the reagents that might be used in such an investigation, ^{29}Si also has the advantage of a natural abundance that is more than twelve times that of ^{15}N and a higher relative (to proton ^{1}H nucleus) sensitivity by a factor of more than seven [29]. Using this concept and proton magic angle spinning solid-state NMR (^{1}H MAS NMR), Brindle *et al.* reported on the interaction of silanes with silicagel [30]. Bauer *et al.* reported work on the characterisation of silane-modified silica particles [31]. Using, among other techniques, MAS NMR as well as NMR in the liquid state for several nuclei (^{1}H, ^{13}C, ^{27}Al and ^{29}Si), they were able to show the disappearance of surface Si-OH, interpreted as formation of bonds between silane molecules and silica. Their conclusions were also in agreement with IR results.

EFFECT OF THE TYPE OF SOLVENT AND CONCENTRATION OF SILANE ON HYDROLYSIS AND ADSORPTION

The time necessary for the hydrolysis of a γ-GPS solution has been recognised as a major variable that must be optimised to ensure an interaction between γ-GPS molecules and the aluminium substrate, as it is generally assumed that the condensation of a hydroxyl functionality with a silanol is easier to perform (on the basis of many considerations such as kinetics of reaction, energy necessary for the reaction, and even steric hindrance of both alkoxy to arrive at, and alcohol produced to leave, the reaction zone) than the same reaction between an alkoxy and a hydroxyl. The hydrolysis reaction may be described as follows:



The reaction is an equilibrium and does not proceed in one step. As shown by McNeil *et al.* [32] for (2-methoxythoxy) phenylsilane, the hydrolysis reaction is completed in three steps, each one faster than the previous, which is attributed to the fact that less steric hindrance is experienced by water as the reaction proceeds. For the ICOSAP project, the reaction was mainly performed in aqueous solution and, therefore, the excess of one reactant, water, displaces the reaction towards the products side in agreement with Le Chatelier's Principle. The initial ICOSAP work concerned with hydrolysis was to establish the hydrolysis time for the recommended 1% concentration of silane in solution. Bertelsen and Boerio initially studied the reaction in deuterium oxide following the conversion of methoxy groups to methanol, or more accurately deuterated methanol [33, 34]. They reported a hydrolysis time of 34 min for a 1% solution (with no change in the aspect of the NMR spectra after 3 h). They also inferred that hydrolysis should happen faster in water due to the slower transfer of deuterium atoms compared with hydrogen. They studied the same reaction for a concentration of 25% GPS in water and reported a time of hydrolysis of between 45 min to 1 h and established that the process was a second-order reaction. If catalysed with acetic acid, the same solution exhibits a much faster rate of reaction, with the completion of hydrolysis occurring between 15 and 30 min. They also showed that the methodology employed for the experiment is important as erroneous, and longer, hydrolysis times may be reported if aliquots are not sampled at regular time intervals, *i.e.*, the reaction is followed from only one initial sampling. Osterholtz and Pohl [35] reported a first-order reaction for hydrolysis reactions of various silanes, but the concentration used was much smaller than in Bertelsen and Boerio's work (0.001 to

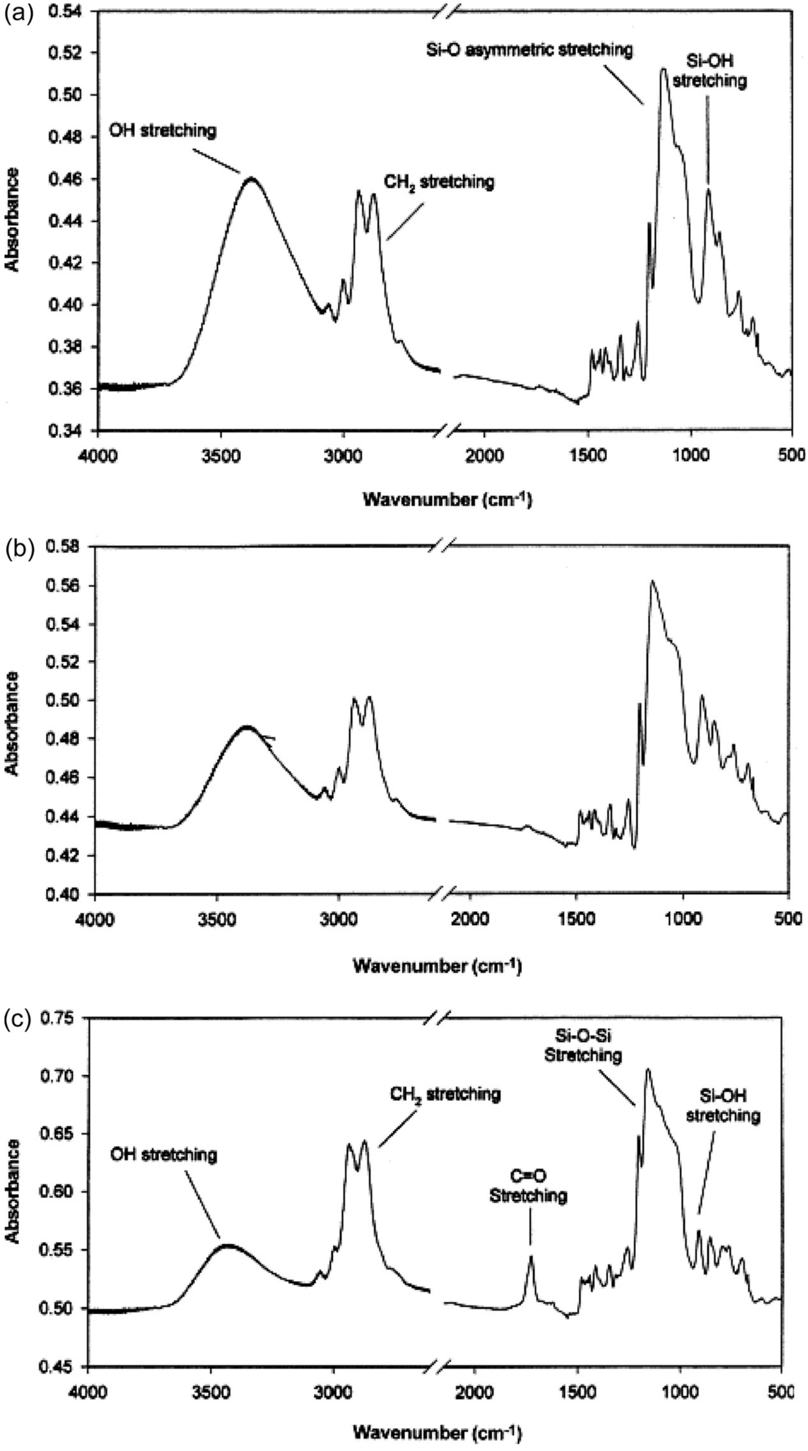
0.03 M) and was also base catalysed. Abel *et al.* [36] also studied the hydrolysis reaction of γ-GPS in aqueous and methanolic solutions. Contrary to the hypothesis of Bertelsen *et al.*, they showed that the hydrolysis of a concentrated solution (8%) happens faster than for the least concentrated and recommended solution used for the ICOSAP programme (1%). They also showed that no significant hydrolysis occurs if the mixture used as solvent contains a major proportion of methanol (90%). This is anticipated as it is in agreement with Le Chatelier's Principle. The hydrolysis times obtained for solution concentrations of 1, 4, and 8% ranged between 50 and 70 min, extremely close to the recommended hydrolysis time indicated by Mazza and coworkers [2]. They also showed the influence of incomplete hydrolysis on the adsorption of γ-GPS on the aluminium surface and reported that the adsorption, or spontaneous interaction, is optimised for aqueous solutions only. An unexpected higher concentration of silicon was reported, by XPS for adsorption on an aluminium alloy, for the solution containing 90% of methanol compared with that of 10%, and this may be assigned to a different conformation in adsorption or deposition of condensed species, forming a weak boundary layer. This is in line with earlier work from the same team in which they showed that the amount of adsorbed γ-GPS silane increases with the amount of water in solution [37].

EFFECT OF TEMPERATURE ON γ-GPS SILANE FILMS

Whenever a silane primer film is deposited on a metallic surface, temperature may be used to improve formation of the bonds between the primer and the substrate. However, the use of elevated temperature to accelerate the drying of the film and improvement of adhesion may itself prove detrimental to the process by creating weaknesses within the primer film. Overcrosslinking or, more simply, a mismatch of modulus between the primer layer and the adhesive film or the substrate may be created and induce premature failure of an adhesive joint; degradation of the reagents used is also possible if too high a temperature is used. Temperature treatment may even induce conformational effects such as the "flip-flop" effect shown by George *et al.* when studying the interaction of γ-aminopropyltriethoxysilane with silicon and pyralin [38]. Using angle-resolved X-ray photoelectron spectroscopy (XPS) to study the interface formed between silicon and γ-APS, they were able to show that the orientation of the silane was changed upon heat treatment (the so-called "flip-flop" effect) from interacting with the amino side to forming covalent bonding with the silanol side.

Bertelsen and Boerio studied the effect of the curing temperature on the chemistry of a γ-GPS film deposited on mirror-polished aluminium coupons [33, 34]. Four temperatures were used: room temperature, plus the recommended 93°C, together with 110 and 180°C. Overall, the increase from room temperature to elevated temperatures up to 110°C indicated mainly a decrease of the OH stretching vibration (3300 cm^{-1}, assigned to water present in the film). Interesting observations were made when the drying temperature is increased to 180°C. This temperature is high enough to drive the water out of the film and cause condensation to occur. The band at 3300 cm^{-1} is greatly reduced, as well as the band at 910 cm^{-1} (assigned to Si-OH stretching) and the band at 1130 cm^{-1}, assigned to Si-O-Si, is shifted to 1152 cm^{-1}. All these are indications of increased Si-O-Si formation, *i.e.*, increased crosslinking density. Additionally, a decrease in the band at 1250 cm^{-1} was assigned to oxidation/degradation of the epoxide ring in a carbonyl C=O species; this assignment is consistent with the appearance of a stretching vibration at 1730 cm^{-1}. This work is a direct illustration of the possible degradation of the chemistry of the film at high temperatures. This is obviously not desirable and, therefore, the recommended temperature for drying a GPS film should be kept below 180°C (or 453 K). Three of these spectra are reported in Figures 3a to 3c for room temperature, 93°C, and 180°C, respectively.

Other authors involved in the same programme, such as Underhill *et al.*, also investigated the effect of curing temperature [39]. Underhill *et al.* studied the effect of the ambient moisture on the sensitivity of the cure by reporting the fractional coverage of cured silane as a function of time and relative humidity using infrared spectroscopy. Silane coatings were deposited on aluminium slides, and after exposure to various conditions of temperatures and relative humidity were rinsed to measure the amount of remaining coverage. It was found that the higher the curing temperature, the more sensitive to moisture the curing phenomenon becomes. The curing process is, however, relatively tolerant of humidity at room temperatures (curing occurs up to 65% RH) and a drastic drop of fractional coverage is only obtained for 95% relative humidity and for temperatures above ambient. Their interpretation of the results, stating that the sensitivity of the silane films to moisture is due to their tendency to form oligomers has, however, to be used with caution. Other factors have to be taken into account, such as the effect of crosslinking on the thickness of silane films if shrinkage occurs, or degradation effects. This work is important in that it shows that ambient humid conditions such as tropical climates will hinder the use of such a repair process unless heat lamps or hot air guns are used.


(a)
Si-O asymmetric stretching
Si-OH stretching
OH stretching
CH$_2$ stretching
Absorbance
0.34 0.36 0.38 0.40 0.42 0.44 0.46 0.48 0.50 0.52 0.54
4000 3500 3000 2000 1500 1000 500
Wavenumber (cm^{-1})
(b)
Absorbance
0.40 0.42 0.44 0.46 0.48 0.50 0.52 0.54 0.56 0.58
4000 3500 3000 2000 1500 1000 500
Wavenumber (cm^{-1})
(c)
Si-O-Si Stretching
CH$_2$ stretching
Si-OH stretching
OH stretching
C=O Stretching
Absorbance
0.45 0.50 0.55 0.60 0.65 0.70 0.75
4000 3500 3000 2000 1500 1000 500
Wavenumber (cm^{-1})

Surface analysis techniques such as ToF-SIMS and XPS were also used to study the effect of the temperature on the interaction of γ-GPS with aluminium using four curing temperatures: room temperature, 50°C, 93°C, and 120°C [40]. Abel *et al.* reported on the effect of this parameter and showed that curing temperatures could be classified in two groups: below 50°C and above 93°C, as indicated in Figure 4. The fragment ions used for the study are assigned as follows: $m/z = 28$ for Si^+, $m/z = 57$ for epoxy fragment, and $m/z = 121$ and 133 for two fragments always present when γ-GPS is adsorbed and of no unique assignment but containing carbon, hydrogen, oxygen, and silicon. It is very likely that the structure of the film is different in these two groups. The reason for the polarisation of the data in this manner is not fully understood and should be the object of further investigation. They also showed that the thickness of the films decreases with increasing temperature (to perform these experiments, the films were deposited with only two minutes brushing so that XPS could be used to assess thickness of coatings). The ratio of the thicknesses of the highest to the lowest is equal to 4 and 13 for initial concentrations of 1 and 4% of silane, respectively. These results were interpreted in terms of increased crosslinking and water evaporation and/or film degradation above 93°C. Evaporation at high temperature of another component should not be overlooked: that of the silane molecules, for example as shown by Mishra and Weimer [41]. They placed clean copper samples in an oven at the same time as silane-coated samples and subsequently observed a Si2p signal by XPS of the originally clean copper samples. This type of evaporation undoubtedly contributes to thinning of the GPS film at the surface of the substrate.

It would be of particular interest to study the effect of the curing temperature of the primer film on the strength of adhesive joints. This has not been performed within the ICOSAP programme as the curing of the adhesive itself (at ~120°C), as well as the postcuring, "hides" any effect of the drying temperature effect on the primer [7]. It is envisaged that further work should be performed using room temperature curing adhesives.

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FIGURE 3 RAIR spectra of a γ-GPS film deposited on 2024-T3 Al from a 1% γ-GPS solution in water and vacuum dried for 24 h at room temperature (a) dried in a vacuum at room temperature for 24 h and then at (b) 93°C for 1 h; (c) 180°C for 30 min in air [34]. Reprinted from Progress in Organic Coatings, Vol. 41, Bertelsen C. M. and Boerio F. J., "Linking mechanical properties of silanes to their chemical structure: an analytical study of gamma-GPS solutions and films," 239–246, Copyright (2001), with permission from Elsevier.

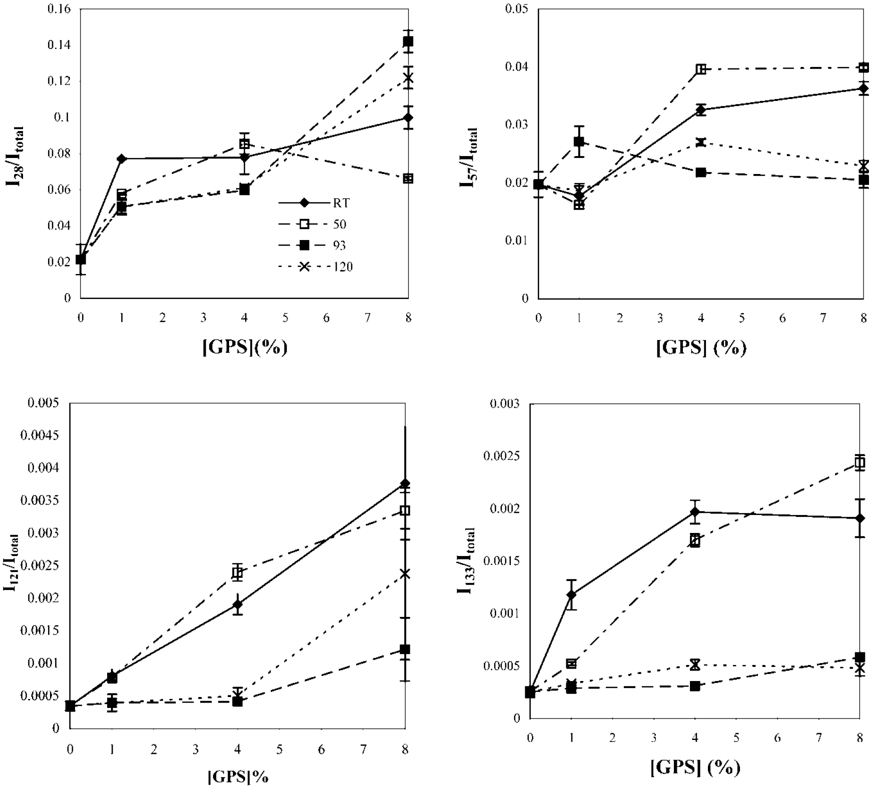
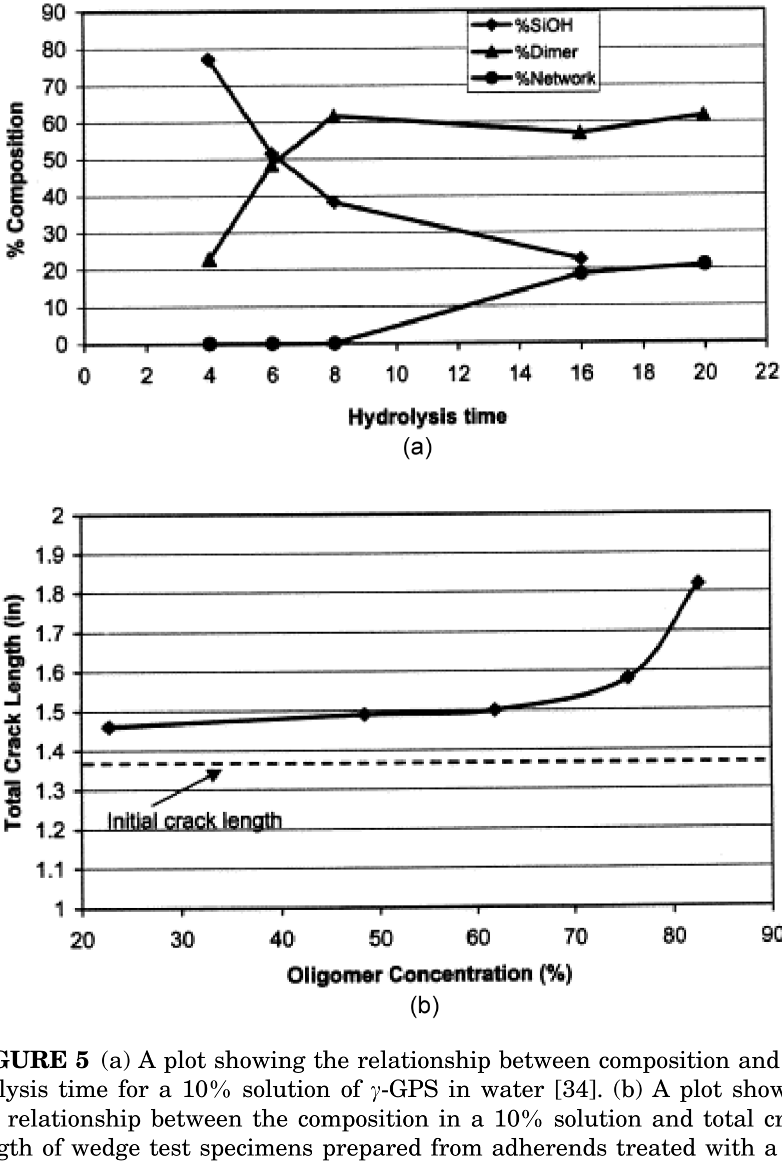


FIGURE 4 Data derived from ToF-SIMS spectra obtained from γ-GPS films dried at various temperatures. The relative peak intensity indicates two types of variations according to the range of drying temperatures: RT and 50°C or 93°C and 120°C, respectively [40].

EFFECT OF THE AGEING OF THE SOLUTION

An important parameter within any process using an organosilane film as a primer is the time between solution preparation and application. The pot life is important and reflects the maximum time after which the primer solution is unuseable as a result of condensation and/or polymerisation. This situation will lead to the fabrication of adhesive joints that will fail prematurely or will not provide the improved strength once tested under harsh and humid conditions.

The failure of the joints is usually attributed to the production of a weak boundary layer *via* the deposition of a primer containing higher than acceptable proportion of oligomers (if not polymers) in the solution. Various articles report on the correlation between time and condensation within the silane solution, but few report both on the solution composition and the related strength of joints. One particularly important study on this topic is reported by Bertelsen and Boerio [34]. Their work, also set within the ICOSAP programme, was concerned with the behaviour of γ-GPS in solution as well as the resulting fracture mechanics performances. They were able to show that for an aqueous solution of GPS at 10% concentration, the concentration of oligomers present in the solution (determined by NMR) can be correlated with the durability of wedge test joints prepared with a 1% GPS aqueous solution. The crack length of the adhesive joints exhibits a sharp increase when the concentration of oligomers in solution is over 60%. This corresponds approximately to 9 h of hydrolysis (65% oligomeric species, including 5% network species) of the aqueous γ-GPS solution. Other scientists within the ICOSAP programme also performed Boeing wedge tests varying the condition of application of the silane solution, and they reached a very similar conclusion in that they advise against the use of a 1% silane solution after more than 10 h of hydrolysis [7]. Figure 5a shows the effect of hydrolysis time of the solution (also ageing time in this case) on the composition of the solution. It is obvious that with increasing time the amount of dimeric and oligomeric species increases, and the use of such a solution to prepare any kind of joint (or even repair process) will lead to premature failure. Figure 5b shows the effect of ageing the solution on the strength of wedge joints. The total crack length of joints prepared with a 1% solution is reported as a function of the oligomer concentration of a 10% solution concentration. This relationship shows that the strength drops for a concentration of just above 60%, which corresponds to an approximate ageing time of 9 h. These results show that the hydrolysis time is a very important parameter because it conditions the pot life of the primer solution but also the optimum time at which to use the solution, *i.e.*, when hydrolysis is completed. For the ICOSAP programme, most of the solutions used where prepared from a solution at pH = 5 or using the natural pH of the water (distilled or MilliQ), a value of approximately 6. According to Pohl and Osterholtz [47], pH = 5 is the value for which the rate of condensation is better controlled or, in other words, when it proceeds the most slowly. This means that the time window for the use of the solution is higher compared with some solutions prepared in an uncontrolled manner. A useful study to be performed would be to proceed to hydrolysis of a more concentrated solution in pH-controlled water and then to dilute the hydrolysed solution in a solvent that may be evaporated easily. This would arrest the hydrolysis reaction and probably increase the pot life of the solution.



(a)

(b)

FIGURE 5 (a) A plot showing the relationship between composition and hydrolysis time for a 10% solution of γ-GPS in water [34]. (b) A plot showing the relationship between the composition in a 10% solution and total crack length of wedge test specimens prepared from adherends treated with a 1% γ-GPS solution [34]. Reprinted from Progress in Organic Coatings, Vol. 41, Bertelsen C. M. and Boerio F. J., “Linking mechanical properties of silanes to their chemical strucure: an analytical study of gamma-GPS solutions and films,” 239–246, Copyright (2001), with permission from Elsevier.

When preparing the wedge test joints, the γ-GPS solution is brushed on the surface. This means that whatever is present in the solution will be deposited on the surface, whether it is hydrolysed silane monomers (or indeed partially or unhydrolysed γ-GPS), dimers, or network structure depending on the time of hydrolysis and the concentration of the silane in solution. However, it is possible to assess whether the chemicals in solution will have an affinity for the substrate by performing adsorption experiments. In unreported data from this laboratory, Abel *et al.* performed such experiments by adsorbing γ-GPS onto aluminium following solution hydrolysis for varying lengths of time (1 to 17 h). Figure 6a reports the amount

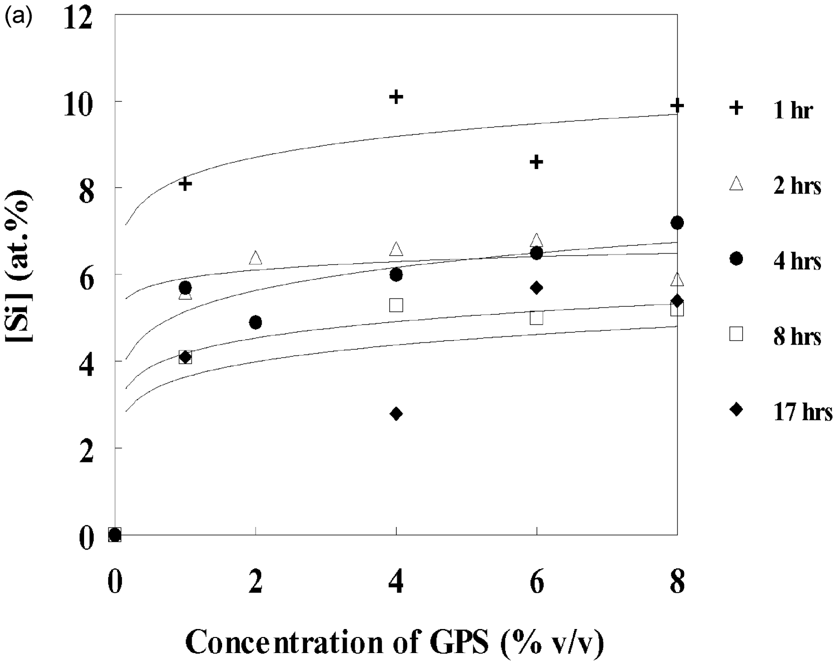


FIGURE 6 (a) XPS adsorption data for aluminium treated with γ-GPS. Various curves were obtained for various ageing times of the solution and indicate a steady decrease of silane interaction with the surface. (b) ToF-SIMS adsorption data obtained from GPS solutions *versus* increasing ageing time of the solution for Si^+ ion. The relative peak intensity is calculated using the intensity of the main ion originating from the substrate Al^+ (m/z = 27). (*Continued*).

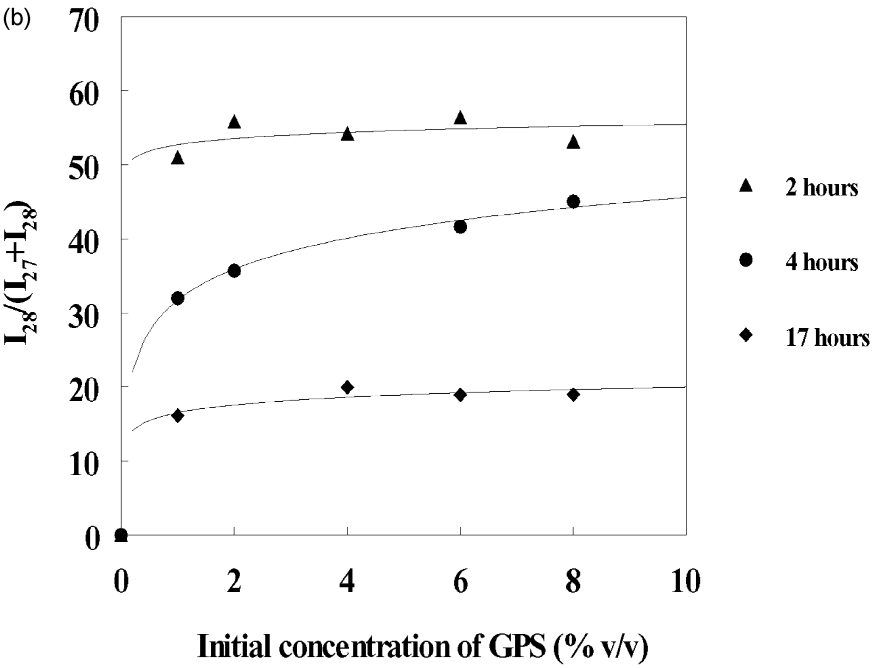


FIGURE 6 (Continued).

adsorbed, as determined by XPS, in terms of silicon surface concentration (atomic%) as well as in relative peak intensity of characteristic fragment ions obtained by ToF-SIMS studies in Figure 6b. It can easily be seen that the amount adsorbed decreases with hydrolysis time, although it always reaches a plateau of adsorption. The obvious conclusion to draw from these experiments is that the greater the concentration of oligomeric species that are present in solution, the less adsorption is obtained on the aluminium surface. This is in total agreement with the data reported by Bertelsen and Boerio [34].

SUMMARY

This review is a clear illustration of the complexity of the influence of the process parameters on the efficiency of a particular primer film based on an organosilane adhesion promoter. However, the effect of many of these parameters makes sense from an intuitive point of view.

It seems logical that covalent bond formation, for example, is correlated to strength and durability of adhesive joints and, whenever possible, may provide a good diagnosis of the process used for repair. This has definitely been shown within the ICOSAP programme, for a number of examples. Optimisation of the parameters for hydrolysis time and ageing time of the solution is also very important and has been shown to be of at least 1 h and less than 10 h at pH 5. Too short a hydrolysis time and the primer does not interact properly with the aluminium, too long and a weak boundary layer is deposited and will provide a weak joint. The effect of the temperature provides a primer film with increased bonding and no degradation and should, therefore, be kept at 93°C or slightly above and at less than 180°C to form bonds between the GPS solution and avoid degradation of the film and subsequent destruction of the epoxy rings, present for interaction with the adhesive. Last, but not least, hydrolysis has to be performed in aqueous solutions or with a little added methanol to provide a primer solution readily available in a relatively short time of 1 h.

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