

**SILANE COUPLING AGENTS
FUNDAMENTALS AND
INDUSTRIAL APPLICATIONS**

8th December 2004



**Society of Chemical Industry
15 Belgrave Square London**

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Programme

- 10.00 Registration and Coffee.
- 10.30 Silanes and their main applications.
J. Monkiewicz (Degussa)
- 11.05 An overview of the international collaborative programme on organosilane coupling agents.
S.Shaw (DSTL)
- 11.40 Test methods and novel silanes for assessing and increasing joint durability.
A.J.Kinloch, K.T.Tan (Imperial College) and J.F.Watts (University of Surrey)
- 12.15 Lunch.
- 13.45 The role of surface analysis in probing the interface chemistry of adhesion and failure of joints involving silane pretreatment layers.
J.F.Watts (University of Surrey)
- 14.20 The Incorporation of Silanes within Formulation: Effect on Durability and Interfacial Chemistry.
M-L.Abel (University of Surrey)
- 14.55 The importance of diffusion and interface enrichment in moisture cure silicone adhesives.
F.DeBuyl, N.E.Shephard, P.Subramaniam (Dow Corning), J.Comyn (University of Loughborough) and T.P.Comyn (University of Leeds)
- 15.30 Silanes as a pretreatment of metals prior to painting.
J.Heitbaum and T.Schmidt-Hansberg (Chemetall)
- 16.05 Discussion,

Close and Coffee.

This one-day symposium is one of an on going series organised by the Society for Adhesion and Adhesives.

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The next symposium is due to be held at the SCI on Wednesday 20th April 2005, entitled "Fatigue and Durability of Adhesive Joints".

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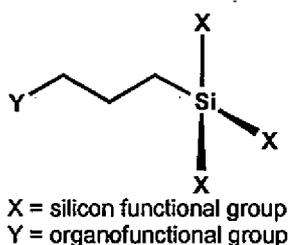
Silanes and their main applications

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Silanes have been used in countless industrial applications with great success for more than 50 years. Many sectors of industry would not be conceivable without raw materials, additives, and auxiliaries based on silanes. The basic large-scale commercial products are tetrachlorosilane and trichlorosilane. Chlorosilanes serve as raw materials for the production of optical fibers, fumed silica, and a variety of electronic materials. Trichlorosilane is used as raw material for the manufacturing of a wide spectrum of organofunctional silanes.

Organofunctional silanes are mainly used as adhesion promoters between inorganic materials and polymers, as surface modifiers of inorganic surfaces and mineral fillers, as crosslinking agents in moisture curing processes, and as comonomers and cobinders in coatings and sol-gel formulations. In practice, organofunctional silanes are applied in aqueous and/or solvent solution as primers or neat as additives.

The properties of standard organofunctional silanes are defined by their bifunctional structure. The silicon as a central atom in the molecule is tightly bound to the organofunctional group Y via a short carbon chain. The organofunctional group Y has to ensure maximum compatibility with the polymer system. On the other hand, three hydrolyzable alkoxy groups X are attached to the Si-atom.



In most applications the mode of action can simply be explained by the following steps: hydrolysis of silicon functional groups X, bonding to the inorganic surface by condensation and reaction with the organic matrix via the organofunctional group Y. Finally, silanes form "molecular bridges" to create stable, water- and chemical-resistant bonds between two dissimilar materials.

The hydrolysis of silanes is strongly affected by their structure, pH, type of catalyst, temperature, solvent, and other factors. Generally, silanes hydrolyze very quickly at a low pH. As a result of the reaction with water, silanol groups replace the alkoxy groups on the central silicon atom. These Si-OH moieties significantly impact the reactivity of a

silane formulation. Silanols are most stable at a pH of 3 - 4 and their reactivity is higher at a pH lower than 2 or higher than 5.

Parallel to the hydrolysis an intermolecular condensation occurs forming oligosiloxane chains. This finally creates an interpenetrating network with a polymer. Initial steps of silane hydrolysis can be monitored by $^1\text{H-NMR}$, whereas the condensation reactions to the Si-O-Si network can be followed by $^{29}\text{Si-NMR}$. The active OH-groups of an inorganic substrate can react with the silanol intermediates and form stable covalent Si-O-substrate bonds. As a consequence, silanes are very effective on substrates with a high concentration of reactive hydroxyl groups, e.g. silica, silicates (glass), oxides, etc. Auger electron spectroscopy (AES) can serve as convenient method for silane film analysis on two-dimensional inorganic surfaces. Oligomeric silanes mostly lead to a more homogeneous silane layer on the surface.

Due to a strong polar character of mineral fillers, silanes are commonly used for organophilic adjustment of the surfaces of mineral fillers. Therefore, in highly filled systems, silanes lead to a strong reduction of viscosity and improve the compatibility with polymers or resins. Novel water-borne multifunctional silane systems create excellent hydrophobic properties of pigments. In situ application of silanes in acrylic resins allows the incorporation of a very big amount of fumed silica in UV-curable formulations, thus increasing the scratch resistance of the final coating.

Alkylsilanes are used for building protection because of their strong hydrophobicity. Special types of alkylsilanes are fluoralkylsilanes. The fluoralkylgroup provides "very low energy" surfaces with extremely poor wettability upon application. Special water-borne formulations based on a fluoralkylsilane are used as permanent protection against graffiti on concrete and other porous substrates. A solvent-based formulation is used for the treatment of glass and ceramics to achieve an easy-to-clean effect. A new product, applied on windscreens, improves the visibility when raining, especially during the night and simplifies removal of insects in the summer. Nanometer-thin coatings based on fluoralkylsilanes show excellent abrasion and chemical resistance and are stable against UV light.

A special oligomeric aminosilane system is used as adhesion promoter for "hybrid" sealants. The non sensitizing adhesion promoter has outstanding properties like reduced VOC, low viscosity and volatility, high flash point, improved film-forming properties, and a high reactivity. Because of its unique oligomeric structure, the new product offers enhanced performance when used in hybrid sealants: improved wet adhesion, low modulus, and high elasticity.

An overview of the international collaborative programme on organosilane coupling agents

Or

ICOSAP – what did it achieve?

M-L Abel, R D Allington, R P Digby, S Millington, N Porritt, S J Shaw, J F Watts et al

The International Collaborative Programme on Organosilane Primers (ICOSAP) was initiated in 1994 with an international workshop at DRA Fort Halstead. What emerged was an international collaborative project (begun in 1996) which eventually involved 16 organisations from six countries (Australia, Canada, France, New Zealand, UK, US). The primary objectives of the programme were to develop pre-bond surface treatments for aluminium providing durability characteristics equivalent/superior to standard anodising techniques (CAA and PAA) with improved environmental sensitivity. The basis of this surface treatment regime was an organosilane, γ -glycidoxypropyltrimethoxysilane.

The organosilane variables studied in the programme were a) nature of the solvent, b) solution pH, c) silane concentration d) hydrolysis time, e) film drying temperature and f) time lag between silane application and bonding. The test specimen employed to study these variables was the Boeing wedge bonded with a rubber-modified epoxy adhesive following the initial silane treatment. All experiments were conducted at 50°C, 95% RH with a maximum ageing time of 168 hours. In addition to measurements of crack growth as a function of time, failed specimens were subjected to both visual examination and more sophisticated surface characterisation based on, for example, XPS and ToF-SIMS.

Results from this large body of tests revealed the optimum silane solution conditions necessary to achieve favourable durability results. These were a) aqueous solution, b) 1% silane concentration, c) pH 5.0, d) 1 hour hydrolysis time. Interestingly, film drying temperature was shown to have an insignificant effect on resultant durability, at least at the temperatures studied. Results using this optimised silane revealed durability levels approximately equivalent to CAA but still inferior to PAA.

Visual examination of the failure surfaces indicated apparent interfacial type failures. However, more detailed investigations using XPS revealed a complex failure zone comprising silane layer, adhesive and oxide layer; the latter observation suggesting a means whereby further improvements in durability could be achieved i.e. modification of the oxide layer. Further tests involving such modifications, followed by application of optimised silane, revealed durability levels, via wedge tests, superior to PAA treatment. Although these are clearly impressive results, it was felt that supporting data, based on other joint geometries, would be necessary to clearly demonstrate the magnitude of this improved performance. Consequently further testing involving both single and double lap joint configurations, subjected to

unloaded ageing and static/cyclic fatigue testing were carried out. Results revealed continual beneficial effects from the improved silane treatment. Steps are now being taken to exploit the results obtained from the investigation.

TEST METHODS AND NOVEL SILANES FOR ASSESSING AND INCREASING JOINT DURABILITY

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Introduction

The durability of adhesive joints upon exposure to an adverse environment has been the subject of concern for many years. Extensive studies [1-2] have been conducted aimed at increasing the resistance to water attack. This may be achieved via the use of a suitable surface pretreatment, such as a chromium-based process. However, growing concerns about the environmental impact of these traditional wet chemical pretreatments has generated interest in ecologically-cleaner alternatives and organofunctional silanes have been widely used as coupling agents to enhance durability of adhesive joints [3-4]. In the present work, the effect of a silane pretreatment on the durability of adhesively bonded joints was investigated.

Experimental

Materials

The substrates used throughout the present work were manufactured either from steel (BS970 070M55), aluminium alloy (BS7075 (unclad)) or toughened soda-lime glass. The adhesive used was a hot-curing rubber-toughened epoxy adhesive, which was based upon a di-cyandiamide-cured diglycidyl ether of bisphenol-A epoxy. Three types of tapered double-cantilever beam (TDCB) metallic joints were made: steel-steel, aluminium alloy-aluminium alloy and steel-aluminium alloy. The last type of joints will be referred to as 'dissimilar-substrate' joints. For glass substrates, double-cantilever beam (DCB) glass-glass joints were made. Two types of silanes were used: γ -glycidoxypropyltrimethoxy silane (GPS) on the metallic and glass substrates; and 22-triethoxysilyl-docos-1-ene silane (i.e. a vinyl-terminated long carbon-chain silane) on the glass substrates. (The glass substrates were used to adsorb the long-chain silane because the glass surfaces are relatively smooth and this should enable the long-chain silane to self-assemble, and so form a monolayer film.) For each silane, the silane solution consisted of 1% w/w of silane, 90% w/w ethanol and 10% w/w deionised water with the pH of the solution controlled to pH 5. The solutions were stirred continuously for an hour before applied to the substrates. Before the application of the silane-based primer, all the metallic substrates were first grit-blasted and degreased (GBD); whilst the glass substrates were cleaned ultrasonically in a bath of deionised water. The silane-coated substrates were then dried at 93°C for an hour. Prior to being bonded, a thin layer of silicone-based release agent or PTFE films was applied onto the substrate surface to create an initial crack. The bond-line thickness of the

epoxy adhesive was controlled during manufacture using 0.5mm diameter wire inserts. The adhesive was cured by heating the joints for two hours at 130°C and then allowing them to cool slowly to room temperature.

Fracture mechanics tests

The metallic joints were tested under monotonic Mode I loading conditions with a displacement rate of the cross-head of the test machine ranging from 0.1 μ m/min to 5 μ m/min. The tests were conducted either (a) at 21 \pm 1°C and approximately 55% relative humidity (RH) or (b) in 'wet' conditions of immersion in water at 21 \pm 1°C. The glass-glass DCB joints were tested in Mode I at a constant displacement rate of 10 μ m/min in the water immersion environment at 21 \pm 1°C.

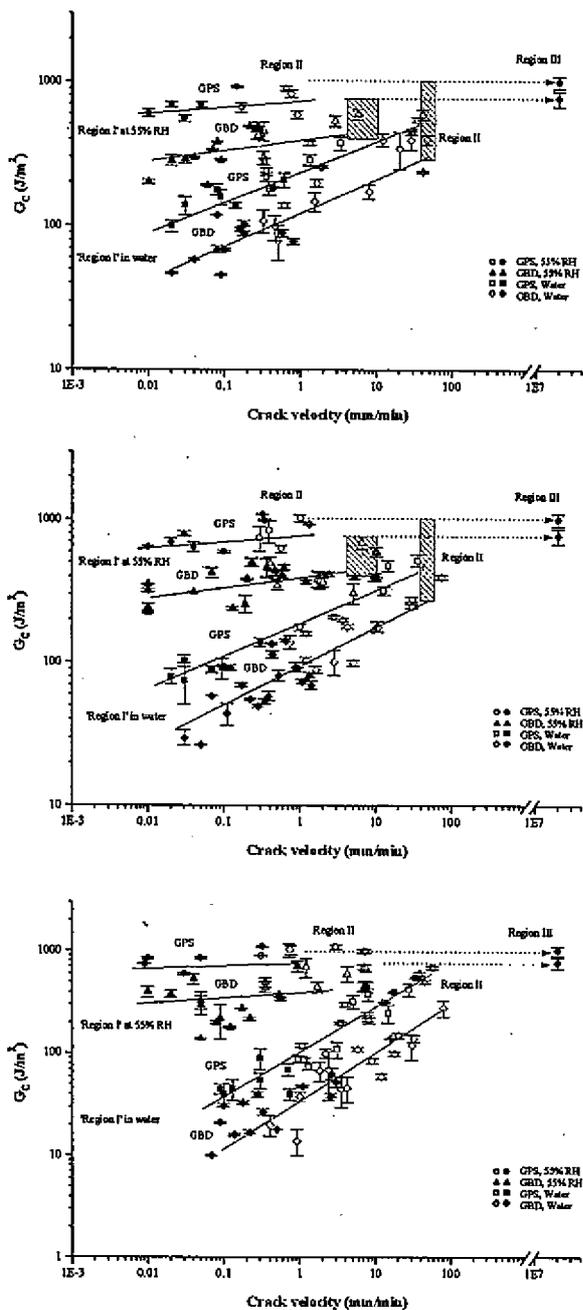
Spectroscopy and microscopy studies

Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) techniques have been used to identify the loci of joint failure and the mechanisms of environmental attack. The SEM study was undertaken using a 'JOEL JSM 5300' microscope. The XPS analyses were undertaken using a 'VG Scientific Sigma Probe' spectrometer. The X-ray source used was monochromatic aluminium K α with a spot size of 50 μ m. Survey spectra were performed with a pass energy of 150eV to detect all peaks, which was followed by high-resolution examination using a pass energy of 50eV.

Results and Discussion

Overview

The values of the adhesive fracture energy, G_C , for the various metallic-TDCB joints were measured in the two different environments as a function of the crack velocity, \dot{a} . The results were plotted on a double-logarithmic scale and the plots obtained for the aluminium alloy, steel and dissimilar-substrate joints are depicted in Figures 1-3, respectively. Three different regions of crack behaviour may be identified, and were labelled as 'Region I', 'Region II' and 'Region III' [5-6]. 'Region I' was observed at low crack velocities and the crack grew in a stable manner, whilst 'Region III' occurred at high crack velocities and stick-slip crack propagation mode was observed and the failure was mainly cohesive in the adhesive. 'Region II' was the transition region between 'Region I' and 'Region III'. The full descriptions of 'Region II' and 'Region III' are given elsewhere [5-6], and only the characteristics of 'Region I' are discussed in detail here.



Figures 1-3. Relationship between G_C and crack velocity for (top) the aluminium alloy joints, (middle) the steel joints and (below) the dissimilar-substrate joints tested in the '55% RH' and 'wet' conditions. 'GPS': GPS silane pretreated joints; and 'GBD': simply grit-blasted and degreased joints. Closed symbols are data collected in the present study whilst the open symbols are quoted from a previous study [6].

Effect of surface pretreatment

The values of G_C for the GPS-pretreated joints are clearly greater than the grit-blasted and degreased (GBD) joints for all types of joint in both test environments. The GPS

pretreatments are known to increase the degree of interfacial adhesion. This increase in the intrinsic adhesion is associated with the formation of covalent bonds between the metallic substrate and silane primer, and in turn between the silane primer and the adhesive layer [3-4]. Therefore, the improvement in the joint durability observed in 'Region I' when using the silane primer was considered to arise from the formation of such interfacial covalent bonds.

'Region I' in '55% RH' tests: Relationship of G_C and \mathcal{A}
 From Figures 1-3 it may be seen that the values of G_C obtained from the '55% RH' tests are not greatly dependent upon the value of \mathcal{A} , and the slopes of the curves are not affected by the surface pretreatment. Therefore, it is evident that, as for the GBD joints [5,7], the relationship between G_C and \mathcal{A} in '55% RH' tests is governed by the viscoelastic relaxation of the epoxy adhesive occurring in the vicinity of the crack tip.

'Region I' in the water immersion tests
 It is noteworthy that the values of G_C for the '55% RH' tests are relatively high at a given \mathcal{A} value, as compared to the 'wet' tests. This clearly indicates the deleterious effect of the water immersion environment. However, it is interesting to note that the slopes of the plots for the 'wet' tests are independent of the surface pretreatment. Therefore, it is likely that the relationship between G_C and \mathcal{A} for the 'wet' GPS-pretreated joints is governed by the same mechanism as suggested previously [7] for the GBD-pretreated joints. Namely, a subtle corrosion mechanism where hydroxyl ions are produced at the cathodic sites, and the presence of these hydroxyl ions at the crack tip is responsible for the accelerated interfacial debonding [8]. However, the mechanism of failure for the GPS-pretreated joints involves the rupture of the interfacial covalent bonds whilst for the GBD joints it involves only the rupture of interfacial secondary bonds. Thus, since relatively higher concentrations of hydroxyl ions would be needed to rupture the interfacial covalent bonds, crack propagation in the GPS-pretreated joints occurs at higher values of G_C as compared to the GBD joints. The occurrence of the cathodic debonding mechanism in the 'wet' GPS-pretreated joints is supported by the greater proportion of the failure that took place in the interfacial regions, as compared to the '55% RH' tests. Moreover, the GPS-pretreated joints in the water immersion tests exhibited inferior durability performance compared to the tests conducted at 100% RH, implying some electrochemical activity taking place in the 'wet' joints. Finally, the occurrence of this subtle corrosion mechanism was reinforced (a) by the physical appearance of the joints after the immersion tests, which appeared to exhibit classical cathodic debonding features and (b) by the good fit of the experimental data to a crack growth model based on the chemical corrosion theory [9]. It is noteworthy that the values of G_C for a given value of \mathcal{A} for the various types of the GPS-pretreated joints re-

vealed that the dissimilar-substrate joints were significantly inferior in durability when tested in water, compared to the similar-substrate types of joint. This observation may again be explained by the same reasoning proposed previously for the 'wet' GBD joints [7]. Namely, firstly, it should be recalled that the mechanism of corrosion involves the anodic dissolution of metal and the cathodic reduction of oxygen. Thus, due to the passivation of aluminium alloy, the corrosion effects on an aluminium-alloy substrate are relatively limited as compared to those on a steel substrate, and thus less oxygen is consumed by the aluminium alloy substrate due to corrosion processes. Secondly, this implies that at the steel/epoxy interface of the dissimilar-substrate joints there will be a relatively high concentration of oxygen available compared to the similar-substrate joints, which would enable the cathodic reactions to proceed more rapidly. Thirdly, this then results in the production of hydroxyl ions at a relatively fast rate on the steel substrate in the interfacial crack-tip regions in the dissimilar-substrate joint. Hence, this causes the cathodic debonding of the adhesive from the steel substrate in the highly alkaline environment to occur at an even lower value of G_C for the dissimilar-substrate joints. ToF-SIMS analyses are currently being undertaken to establish this hypothesis.

Long-chain silanes as adhesion promoters

As is evident from Table 1, the GPS-pretreated glass-glass joints exhibited better durability performance than the ultrasonically-cleaned joints. Now, it has been reported [10-11] that the silane performance might be improved further if the silane could be adsorbed as an ordered monolayer; in such a way that the hydrocarbon chains are densely packed together and with epoxy end-groups available for reaction with the epoxy adhesive. To explore this aspect, the potential of a novel long-chain self-assembling silane (with twenty $-CH_2-$ groups) to improve joint durability is being investigated. It involves the synthesis and establishment of monolayer films of the adsorbed vinyl-terminated long-chain silane on the glass substrate. As may be seen from Table 1, the values of the measured G_C for the vinyl-terminated long-chain silane pretreated joints are relatively low, implying that the vinyl-terminal groups are indeed uppermost, and so adjacent to the epoxy adhesive. However, to enable covalent bonding with the epoxy adhesive, these vinyl-terminal groups need to be 'activated' to form epoxy-terminal groups via a series of chemical reactions. Such experiments are currently being undertaken.

Table 1. The measured values of G_C for various types of DCB glass-glass joints tested at 10 μ m/min in water.

	Specimen 1 G_C [J/m ²]	Specimen 2 G_C [J/m ²]
Ultrasonically-cleaned joints	59.0 \pm 21.3	59.5 \pm 16.4
GPS-pretreated joints	96.8 \pm 10.3	86.3 \pm 3.7

Vinyl-terminated long-chain silane pretreated joints	< 11.0	< 11.0
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Conclusions

The fracture behaviour of GPS-pretreated metallic TDCB joints was investigated over a range of displacement rate and in two environments, i.e. at 55% RH and immersion in water. In both environments, the use of the silane primer has been seen to improve the joint durability. This is suggested to be due to the formation of interfacial covalent bonds. From the plots of $\log G_C$ versus $\log \dot{\delta}$, it was found that the slopes of the curves for the GPS-pretreated joints were similar to the simply grit-blasted and degreased (GBD) joints in both environments. Therefore, it is suggested that the relationship between G_C and $\dot{\delta}$ in the '55% RH' tests was governed by the viscoelastic nature of the adhesive, whilst the joint fracture in water was controlled by the mechanism of cathodic debonding. ToF-SIMS analyses are currently being undertaken to establish such hypotheses. The potential of using a long-chain self-assembling silane (with twenty $-CH_2-$ groups) as an adhesion promoter was also investigated. The relatively very low value of G_C ascertained with the vinyl-terminated long-chain silane pretreated joints is encouraging, as this indicates that the silane has adsorbed with the vinyl terminal groups uppermost, and so adjacent to the adhesive layer. Work is currently being undertaken to convert *in-situ* the vinyl terminal groups into epoxy terminal groups.

Acknowledgements

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The Interfacial Chemistry of Adhesion: Surface Analysis and Organosilanes

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In adhesion research there are a variety of fundamental parameters that need to be addressed, these include the areic density of bonding sites at the interface and the type of bonds that are formed. Given that the interface in any technologically important system is buried many micrometers, if not millimetres, by both substrate and organic phase this is a particularly tall order. As the distances over which the forces of adhesion operate are very small (of the order of nanometres) any chemical analytical technique to be used must have an analysis depth commensurate with this length scale. Access to the buried interface is difficult and it is unlikely that examination of the locii of failure following a mechanical test will provide the required region of the interface for analysis.

This presentation will address these problems in some detail based on research carried out at the University of Surrey. The surface analysis methods of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) will be introduced and the state of the art in current instrumentation will be described. There are interesting parallels between the developments that have occurred in XPS and ToF-SIMS instrumentation and the nature of the solutions that can currently be provided in adhesion research. Much of the work being carried out at the current time would not have been attempted 10 years ago!

The bulk of the talk will review methods in which analysis of the buried interface can be achieved. Such approaches range from the simple expedient of forensic analysis of failed joints, which sometimes provides the required solutions, through to the use of model samples and the "unravelling" of complex formulations to enable the manner in which individual components interact with the substrate surface. Much work has been carried out using organosilane pretreatments and examples will be given contrasting the interaction of molecules from commercial adhesives with silane treated and bare aluminium. The construction of adsorption isotherms from XPS/ToF-SIMS data is particularly useful in these types of investigations and the methodology will be described in full. Mechanical and chemical section can also enable the interface to be approached without the disruption associated with mechanical perturbation. In addition there is much merit to using an imaging technique for the analysis of failure surfaces. Recent results using imaging XPS for the analysis of failure interfaces from adhesively bonded aluminium will explore the possibility of using such a technique whilst retaining the advantages of traditional XPS.

The Incorporation of Silanes within Formulation: Effect on Durability and Interfacial Chemistry

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The use of organofunctional silanes as primers for adhesive bonding has increased in recent years as a result of the potentially harmful environmental impact of the traditional pretreatment methods for aluminium for adhesive bonding [1]. A procedure involving the application of a 1% aqueous solution of γ -glycidoxy propyl trimethoxy silane adhesion promoter (GPS) on aluminium, followed by drying at elevated temperature has been shown to have much to commend it for repair purposes. The formation of a covalent bond via condensation between hydroxyls present at the surface of the metal and silanols of the hydrolysed silane [2] is a well accepted prediction and it has indeed been proven on iron and other metals for various silanes mainly by SIMS [3, 4, 5]. It is now also been established for aluminium and the improved durability is attributed mainly to the formation of covalent bonds via condensation between hydroxyls present at the surface of the metal and silanols of the hydrolysed silane [6].

Organosilanes are also used in many adhesive and paint formulations, partly to avoid the need for the application of a primer. This is probably the most promising and cost effective manner of employing them for adhesive bonding, but also the least well understood. Most manufacturers will add small amounts of an organosilane to their formulation on an *ad-hoc* basis. The efficacy of this is not proven, and the mode of action, if beneficial, is not well understood. However, as one step is eliminated in the production process, the production costs and environmental effects are reduced still further compared with traditional pretreatments. The next step in silanes research on silane behaviour and joint performance is to undertake a more fundamental study on the mode of action of these molecules when incorporated within any formulation and investigate for the effect of various parameters such as concentration and chemistry of silane, type of substrate and treatment (curing, melting) temperature.

In this work we describe results on the durability and interfacial chemistry of Boeing wedge tests prepared using an adhesive with varying amounts of silane in a commercial two-part epoxy paste adhesive formulation (from 0 to 2% wt of silane). Durability results indicate an improvement upon incorporation of an epoxy type silane and surface analysis (performed mainly by XPS) sheds light on the segregation of the silane at the interface when present in the formulation as well as the depletion of curing agent for the adhesive without silane. Another example of the use of silanes within a system as opposed to a primer will be provided when incorporating γ -amino propyl trimethoxy silane (APS) within a polyamide coating on steel. It will be shown that the durability of the coating is improved, segregation occurs and bonds are formed between the APS in the coating and the steel [7]

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The importance of diffusion and interface enrichment in moisture cure silicone adhesives

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Abstract

When an alkoxy silicone sealant is exposed to ambient air, a surface skin is formed, which becomes thicker with time. It has been observed that, at constant temperature and humidity, the thickness (cure depth) is initially proportional to the square root of time, but later the gradient of such a plot increases. There are thus two regions of cure, an outer region and an inner one. Swelling in toluene and functionality testing, which has been measured for samples taken at various depths, shows that the crosslink density is greater in the outer regions. Single lap joints in aluminium or glass have been cured in these two regions and joints from the outer region are always stronger than corresponding ones from the inner region. Tensile adhesion joints on glass shown also a change from an "interfacial" to a cohesive failure mode as we move from the inner to the outer region of the joint. Similarly, Young's modulus is also greater in the outer regions. These behaviours are all due to the mobility of the low molecular weight silane and titanium ester species used as crosslinking agents and adhesion promoters. During the initial stages of curing process they migrate into the outer region of the joint, but once cure has passed into the inner region there is now a paucity of these compounds. We also have shown that the extent of silane migration is influenced by their initial concentration made available in the system.

Introduction

The diffusion of small molecules through polymer materials plays a crucial role with respect to almost all physical properties of coatings, adhesives and sealants ^[1].

Recently, interesting studies have been carried out to understand interfacial structures of organosilanes at the molecular-level in polymers materials using sum frequency generation (SFG) vibrational spectroscopy [2, 3, 4]. In those studies, the authors demonstrated that silanes molecules, e.g., 3-aminopropyltrimethoxysilane (ATMS), n-octadecyltrimethoxysilane (OTMS), and n-octadecyltrichlorosilane (OTCS), can adopt very different conformations while contacting different polymer surfaces, e.g., poly(methylmethacrylate) (PMMA), polystyrene (PS), and poly(ethyleneterephthalate) (PET). Understanding how molecular structures of interfaces between polymer materials is very much desired because these are the interfacial properties that play a crucial role in numerous applications, e.g., in any adhesive system, anti-fouling coatings, microelectronics assembling, photonics, and biology [4, 5, 6]. Furthermore, the kinetics of diffusion of of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATM) into PMMA have been deduced from time-dependent SFG signals characteristic of the silane molecules as they were diffusing through polymer films of different thickness [2]. According to the Fickian model, the diffusion coefficient of AATM in PMMA was calculated being $(3.80 \pm 0.39) \times 10^{-13} \text{ cm}^2/\text{s}$.

In the present study, using a quite different experimental approach we investigated the diffusion of silane and titanium ester molecules across a thick layer of silicone sealant adhesive applied on aluminium or glass. The primary reason for carrying out this work was the observation that a room temperature vulcanisation (RTV) alkoxy silicone sealants [7], applied on glass in a standard weather-sealing joint, was showing an outer zone where failure is within the sealant, but in the centre there is interfacial failure between sealant and the substrate [8].

Results and discussion

The details of experimental conditions and a complete description of the system studied that we discuss below can be found in recent publications by the present authors [8, 9]. Basically we have measured the depth of cure (z) at constant static humidities and temperatures using sealant placed in small cylindrical containers of various total depth (7, 11, 17 and 48mm). We observed that plots of z against the square root of time show distinct outer and inner regions, with an intervening kink. For the 7, 11 and 17mm depth containers the time at which the kink occurs increases proportionally with depth. An explanation for this phenomenon is that the reactive

silane molecules, i.e., methyltrimethoxysilane (MTMS) and isobutyltrimethoxysilane (IBTMS) used as crosslinking agents, and tetra-tert-butyl titanium ester (TTBT) used as condensation catalyst are diffusing to meet the advancing cure front, where they immediately react with water, hence slowing down the rate of cure^[8]. The curing reactions depend therefore on the diffusion coefficients of, respectively, the silanes and titanates in the uncured sealant, which some of these have been measured. The value of the diffusion coefficient was found being, $D = 1.3 \times 10^{-11} \text{ m}^2/\text{s}$ for TTBT, constant for the whole duration of the experiment, and $D = 6 \times 10^{-11} \text{ m}^2/\text{s}$ for IBTMS initially, which later decreased with the duration of the experiment, likely due to the interaction of the silane with the fumed silica particles used as reinforcing filler in the sealant^[9].

This prompted us to measure physical properties of the cured sealants from various depths from the air-exposed surface for understanding the effect of these diffusion phenomena on the ultimate cured sealant properties. Young's modulus, concentration profile of the silane crosslinks, swelling in toluene, and adhesion to aluminium and glass in the inner and outer regions, respectively, were measured.

The Young's modulus, E , values calculated for the samples 1 through 7 dissected from a Tensile-Adhesion (TA) joint (Figure 1) are shown in Figure 2. The E values exhibit a gradient, with a minimum through the cross-section of the sample, and maxima at the two ends. However, the modulus corresponding to the sample dissected from the air-exposed end is significantly lower than the adjacent layer, in addition to being oddly out-of-trend with the shallow U-shaped gradient for the modulus values through the cross-section of the joint.

The shape of the crosslinking density across the depth of cure of a similar TA joint measured by swelling in toluene shown in Figure 3 are similar in shape to that of the modulus gradient shown in Figure 2, with the exception of the end at/near the air-exposed surface. This behaviour can be explained as follows: It is possible that the excess moisture available at the air surface causes excessive reaction of the crosslinker and other smaller components, in a manner that could lead to insufficient crosslinking of the polymer ends. This would result in lower modulus values at/near this surface, as has been measured in the samples studied.

Similarly, the concentrations of crosslinker residue determined by crosslink density measurements across the cross-section of the TA joint are showing a gradient (**Figure 4**), with maxima at the outer ends of the joint, and a minimum through the middle. It is also seen from these curves that the extent of crosslinker migration is influenced by the initial amount of crosslinker made available in the system, i.e., higher the initial concentration of crosslinker, higher the amount of crosslinker residue at the outer ends of the joint, and deeper the shape of the gradient curve.

Curing of the sealant in the shape of a TA joint involves diffusion of moisture via the two outermost surfaces (or interfaces) – one exposed to air, and the other semi-permeable. As moisture diffuses into the sealant material at the two ends, it results in a number of chemical reactions including the consumption of crosslinker species at/near the outer ends of the joint. This is accompanied by the reaction of polymer ends resulting in a crosslinked polymer network, i.e., cured network with a higher modulus, *E*. As the crosslinker species at/near the surfaces of the joint are consumed, a gradient in the concentration of this species is created, with depletion at the outer ends. This concentration gradient can favour the migration of the low molecular weight and relatively mobile crosslinker species, from the middle of the joint towards the depleted ends. It also follows that the crosslink density, and thereby the modulus values for the samples dissected from the outer ends of the TA joint will therefore be higher than those from the middle of the joint. In other words, the shape of the gradient in modulus values across the cross-section of the TA joint is expected to be similar to that of the gradient in crosslinker residue content through the joint – with maxima at the two ends and passing through a minimum in the middle of the joint.

One further aim of this study was to see if adhesion of sealants to aluminium and glass differed between the outer and inner regions in a 17mm tub. This involved making single lap joints and curing them in 17mm tubs filled with sealant as illustrated schematically in **Figure 5**. In 17mm tubs the kink which separates the outer and inner regions is located about half way down. Details of the experimental set-up is described elsewhere [8].

Mean joint strengths with standard deviations and modes of failure are shown in **Table 1**. These show that joints taken from the outer regions are stronger than those

taken from the inner regions. Also, there is a significant tendency with aluminium joints for the mode of failure to be cohesive in the upper regions, and to have an interfacial component in the lower regions.

Table 1: Testing of single lap joints

Temp °C	r.h. %	Joint strengths (N) with mode of failure			
		aluminium-aluminium		glass-glass	
		inner region	outer region	inner region	outer region
5	100	196 ± 36 C*	283 ± 20 C	255 ± 41 C	339±47 C
25	75.4	167 ± 52 I	292 ± 18 C*	232 ± 68 I*	344±54 I
35	100	115 ± 13 I+C	257 ± 39 C*	272 ± 23 C	304±24 C

Failure modes are shown by the following codes. C = 100% cohesive failure, C* = dominantly cohesive failure. I = 100% interfacial failure, I* = dominantly interfacial failure, I+C = mixed failure.

Conclusions

Our present study has focused on understanding how gradient of physical properties occur in an adhesive joint due to diffusion phenomena of the low molecular weight reactive components, instead of looking at the molecular-level of the phenomenon as described earlier in the introduction. We have shown the importance for taking into account the role of diffusion of silanes and titanium ester, and therefore the enrichment of these species at the interfaces for understanding and predicting the behaviour of an adhesive in contact with, respectively, the ambient air and the substrates in a sealing application. However, both approaches are extremely useful for establishing more broadly the relationships between the structures and concentrations of chemical species at polymer/substrate interfaces with macroscopic physical properties of the assembly.

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Figures

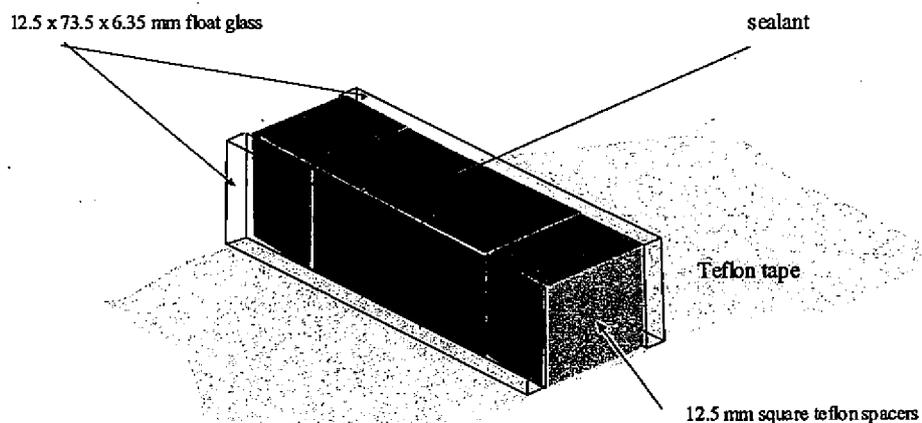


Figure 1: Mode of preparation of Tensile-Adhesive joint using Teflon® tape.

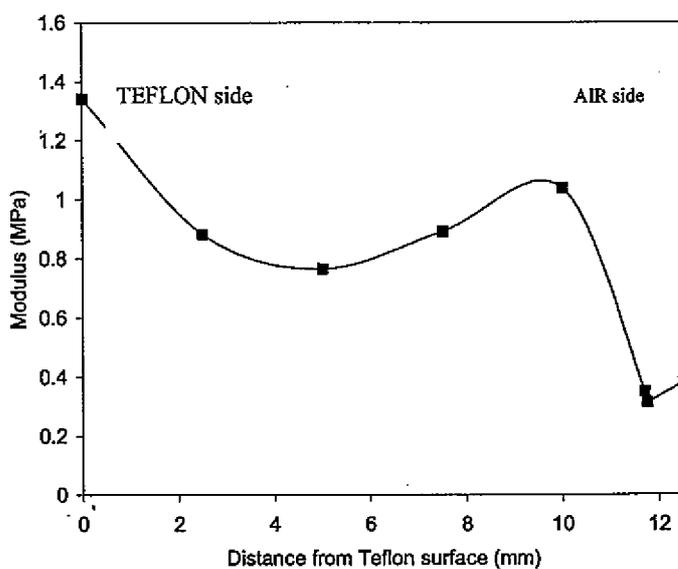


Figure 2: Young's modulus of cured sealant from different depths in a glass joint.

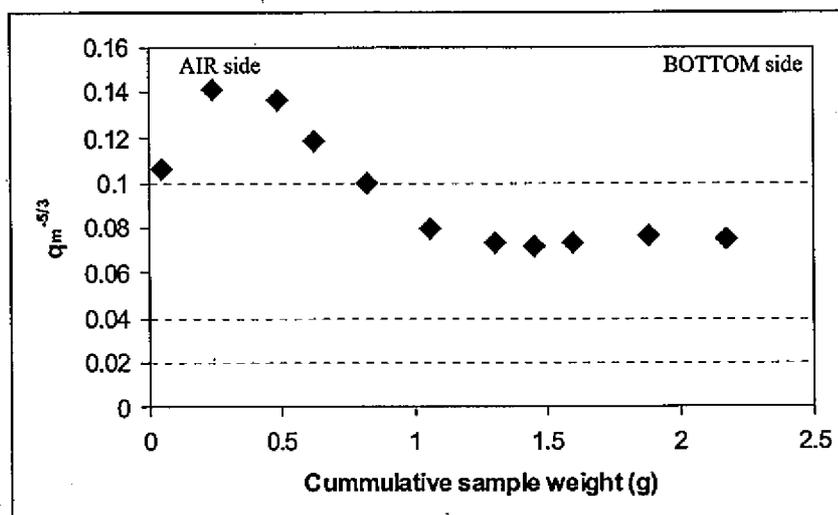


Figure 3: Crosslink density measured by swelling in toluene of sealant cured at 75.4% r.h. and 25°C.

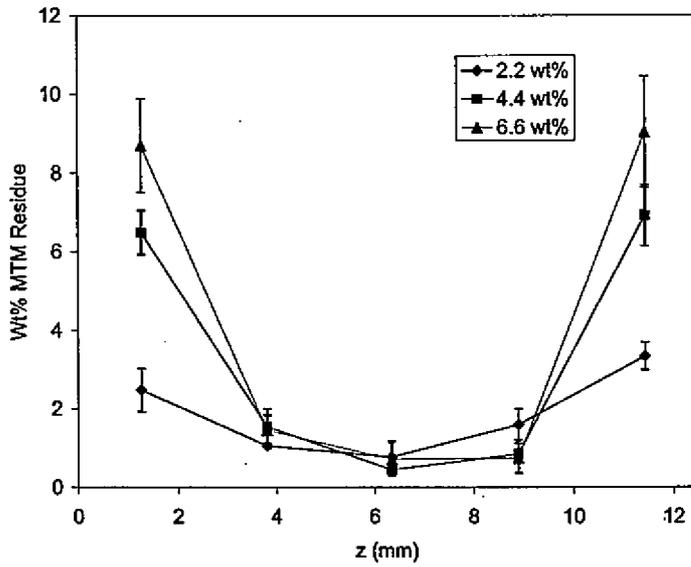


Figure 4: Concentration profiles of MTMS across sealant cured in a glass joint. Initial concentrations of MTMS were \blacklozenge 2.2%, \blacksquare 4.4% and \blacktriangle 6.6%.

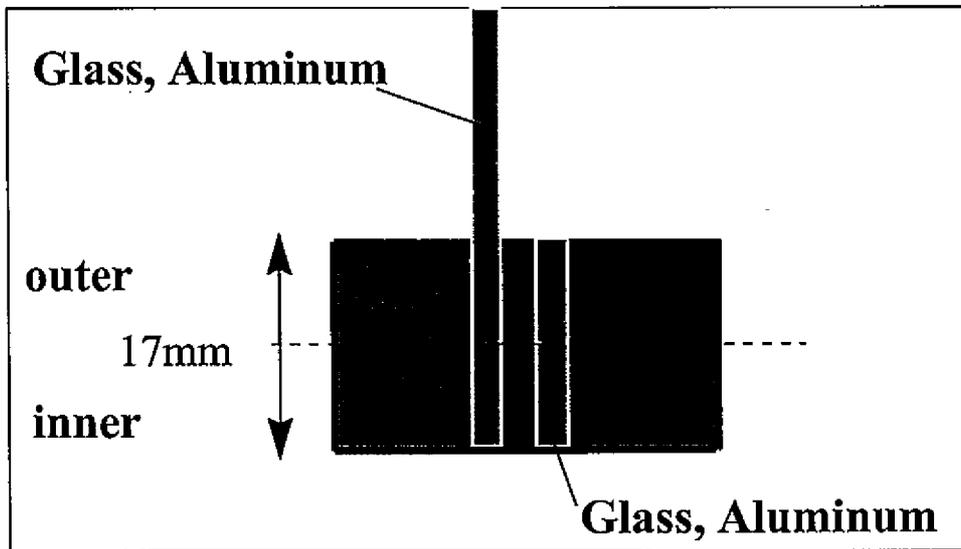


Figure 5: Schematic representation of lap shear joint (either aluminium or glass) prepared in the 17 mm depth container.

Silanes as a Pretreatment of Metals prior to Painting

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The use of Silanes as Coupling Agents and Adhesion Promoters is well established with numerous uses in additives for adhesives, sealants and paints. Therefore it is not surprising that silanes have, for some time, been discussed¹ for use in anti-corrosion coatings and prior-to-painting pretreatments. The advantages of silanes are numerous: they have multi-metal capability as they are able to attach themselves to all metals used in industry such as steel, galvanized steel, aluminium, magnesium, titanium, etc, where they can be applied by spray, dip, roll coating, rinse or dry in place processes when incorporated into aqueous solutions. Silane solutions are in essence metal-free and especially do not contain carcinogenic chromates or nickel compounds. Thus, one only might wonder why silanes are not yet used throughout the industry.

There are several reasons why this has been difficult to achieve. First of all the appropriate silanes have to be selected as typically mixtures of functionalised monosilanes and di-silanes have to be carefully selected. Secondly, since the industry is accustomed to treat parts and strip with aqueous based products and since silanes need to be applicable in the existing pretreatment lines, hydrolysis of the silanes has to be taken into account and the question of how to develop stable concentrates has to be answered. Thirdly the coating formation needs to be optimised. Specifically this means bringing the substrate into the appropriate surface state by choosing the right cleaning, pickling and conditioning steps prior to the formation of the silane layer.

Today these difficulties have been overcome and we shall present the latest results on the following topics:

- Raw materials for silanes pretreatment
- Hydrolysis and nature of products
- Coating formation
- Surface preparation for silane treatment
- Existing OXSILAN[®] product range and quality under paint
- New developments and future applications

It is our aim to demonstrate to the audience that silanes based technologies are a viable alternative to traditional surface treatment processes.

¹ W. J. van Ooij and T. F. Child, CHEMTEC 28, 26 (1998); V. Subramamian and W.J. van Ooij, CORROSION, 54, 204 (1998)