Self-assembling monolayer silane films as adhesion promoters

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The structure of adsorbed silane films formed by the adsorption of trichlorosilane molecules containing long alkyl chains from solution onto aluminium substrates has been investigated. The structure of the adsorbed films is dependent on the alkyl chain length. When the chain length is equal to or greater than 18, the molecules form a film in which the hydrocarbon chains are densely packed together and orientated away from the substrate. As the chain length is reduced the films become progressively more disorientated. When a terminal vinylic group is present on the molecules, the films can be activated after adsorption to yield a hydroxyl group that is available for further reaction with a polyurethane resin. The ability of 10-undecenyltrichlorosilane and 18-nonadecenyltrichlorosilane to act as adhesion promoters has been investigated using the blister test. Both these silanes yielded adhesive fracture energies of 18 J m^{-2} under dry conditions. When water was present, only the joints pretreated with 18-nonadecenyltrichlorosilane exhibited a high resistance to moisture attack. In these joints the dense packing of the hydrocarbon chains impeded the diffusion of water to the interface. In the case of the adsorbed 10-undecenyltrichlorosilane films, the disorientated nature of these films allowed the water to reach the interface more easily, resulting in rapid joint failure.

(Keywords: adhesion; silane; monolayers; blister test; durability)

INTRODUCTION

Silanes have been used for many years to improve the durability of structural adhesive joints and have been shown to be effective on a wide range of substrates[1–5]. These chemicals possess the general chemical formula $R'\text{-}Si(R)_3$ where R' is usually a short carbon chain containing some additional chemical functionality capable of reacting with the adhesive resin. R is a hydrolysable end-group such as an ethoxy, methoxy or chloro group which can react with water present, either in the pretreatment solution or adsorbed on the surface of the substrate. This reaction forms silanol (Si–OH) groups. The theories that have been proposed to explain the effectiveness of silanes in improving the durability of structural joints have been reviewed by Plueddemann[6] and so only the two most commonly invoked theories, the 'covalent bonding theory' and the 'reversible hydrolysis theory' will be discussed here. In fact, the reversible hydrolysis theory can in many ways be regarded as a refinement of the covalent bonding theory.

The covalent bonding theory proposes that the silanol groups initially react with the hydroxyl groups present on the surface of the substrate to form interfacial covalent bonds. Subsequent adsorption results in the silanol groups condensing with each other to form a polysiloxane (Si–O–Si) network. Finally, the additional functionality present on the silane group reacts with the adhesive forming silane/adhesive covalent bonds. Thus, a continuously bonded 'bridge' between the substrate and the adhesive is formed and the covalent bonding theory postulates that this bonded 'bridge' is responsible for the improvement in the durability of silane pretreated joints. Evidence supporting the formation of interfacial Si–O–M bonds where M is Fe, Cr, Al, Pb, Ti and Si has been published[7–12]. The interaction between the adhesive resin and the functional group has also been investigated[13–15] confirming that the additional functionality present on the short carbon chains can react with the adhesive.

The main problem with the covalent bonding theory is that, as Plueddemann[16] has pointed out, the Si–O–substrate and also Si–O–Si bonds are not truly covalent, but contain a high proportion of ionic character. For example, using the method proposed by Pauling[17] to calculate the degree of ionic character, the Si–O and Al–O bonds actually contain 54% ionic and 64% ionic character respectively. Plueddemann argues that such a high proportion of ionic character is likely to render the interfacial Si–O–substrate and Si–O–Si bonds susceptible to attack by moisture and the formation of the bonded 'bridge' cannot solely explain the increase in durability of silane pretreated adhesive joints. Plueddemann has therefore proposed the 'reversible hydrolysis theory' to explain the mode of action of silane pretreated joints. In this theory, the Si–O–Si and Si–O–substrate bonds can be hydrolysed, but this process is reversible. This

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process is illustrated for the Si–O–Si bonds in equation (1).

$$R_3\text{–Si–O–Si–}R_3 + H_2O \leftrightarrow 2R_3\text{Si–OH} \qquad (1)$$

As the hydrolysis reaction is reversible, for a given set of reaction conditions, the concentrations of the various species will be in equilibrium with each other. From Le Chatelier's principle, if the concentration of water increases, the equilibrium will change in order to remove the extra water from the system. This will clearly involve a shift towards the right-hand side and thus the breakage of the Si–O–Si bonds. However, Plueddemann argues that the silanol groups are continually forming and then recondensing and that the improved durability of the silane pretreated joints is a result of this mechanism. If this theory is correct, it would be expected that the durability of silane-pretreated adhesive joints would improve if the number of interfacial Si–O–substrate bonds and the cross-link density of the polysiloxane network could be increased. This would mean that the number of bonds that needed to be broken before failure could occur would increase. More water would therefore be required to reach the interface in order to drive the equilibrium in equation (1) far enough to the right-hand side to cause joint failure. As the time required for the increased concentration of water to diffuse to the interface would increase, the joint durability would therefore also increase.

However, a third way to improve the durability is by simply preventing water from reaching the interface. In theory, this could be done by increasing the number of hydrocarbon chains in the adhesive, thus reducing the polar nature of the adhesive. For many applications, this would result in a loss of other properties of the adhesive. For example, possibly an unacceptable loss of joint strength and perhaps more importantly, a reduction in the high temperature resistance of the joint. A more attractive alternative was investigated by Jang *et al.*[18]. These workers attempted to decrease the polar nature of the silane film itself by grafting long hydrocarbon chains of varying length onto an acrylic based trimethoxysilane. These silanes were then used to pretreat the glass used in glass reinforced polyester laminates and castings. While some improvements in both the initial adhesion and durability were noted, no clear correlation between the durability and the length of the hydrocarbon chain was observed.

The concept of increasing the hydrophobicity of an adsorbed silane film as a method of improving the durability is interesting. One way in which truly hydrophobic monolayer films can be formed on solid substrates is by the use of self-assembling molecules[19–28]. Self-assembling molecules consist of a polar head-group, for example a carboxylic acid, amine or trichlorosilane group and to this head-group is attached a long hydrocarbon chain, usually possessing a methyl terminal group. These molecules adsorb spontaneously from solution to form monolayer films in which the head group is adjacent to the substrate and the long hydrocarbon chains extend away from the substrate. Contact angle measurements[19–21,23–25], ellipsometry[20,21,23–25], electron diffraction[27] and reflectance infra-red spectroscopy[22,23] have been used to study the adsorbed films. This work has shown that for a particular substrate/head group combination, a critical chain length exists where the hydrocarbon chains can pack closely together resulting in an outermost surface which consists of densely packed methyl groups. Ellipsometry studies have shown that the films are monolayer films and the electron diffraction and infra-red studies have shown that the hydrocarbon chains are generally orientated either vertically or at an angle of approximately 30° from normal to the surface of the substrate.

The work of Netzer *et al.*[25,26] is of the greatest interest as these workers studied the adsorption of vinylic terminated trichlorosilanes with a range of chain lengths of up to 16 carbon atoms onto glass, silicon and evaporated aluminium mirrors. In order to assess the influence of the terminal vinylic group on the adsorption of the films, these workers also investigated the adsorption of octadecyltrichlorosilane. The workers found that as the vinylic group was non-polar, it did not interfere with the adsorption of the films. However, they did discover using contact angle measurements, ellipsometry and reflection adsorption infra-red spectroscopy, that the octadecyltrichlorosilane films were of higher quality than those formed by the longest vinylic terminated trichlorosilane studied, namely, 15-hexadecenyltrichlorosilane. These workers therefore concluded that on aluminium, a chain length of at least 18 was required for the formation of the highest quality films.

The advantage of the terminal vinylic group is that it can be 'activated' after formation of the film, via a hydroboration reaction using diborane followed by oxidation using alkaline hydrogen peroxide, to form a terminal hydroxyl group. While these workers utilized this property to re-adsorb a further silane layer, thus forming a multilayer, these molecules are capable of acting as adhesion promoters, as the hydroxyl group is available for reaction with an adhesive resin such as a polyurethane. In addition, by pretreating the activated film with epichlorohydrin, an epoxy terminal group could be created, allowing the adsorbed film to react with amine-based epoxy curing agents.

The current work is concerned with the evaluation of these adsorbed long-chained vinylic terminated trichlorosilanes as adhesion promoters. This research has investigated the structure of films formed by the adsorption of methyl terminated trichlorosilanes with chain lengths ranging from six to 20 onto both evaporated aluminium mirrors and alkaline etched British Standard (BS) 1200 grade aluminium alloy substrates. The reaction pathway used to synthesize the two vinylic terminated silanes, 10-undecenyl and 18-nonadecenyltrichlorosilane, has been summarized and the structure of these adsorbed trichlorosilane films was also studied. The ability of these vinylic terminated trichlorosilanes to act as adhesion promoters was investigated using the blister test. This test allowed the adhesive fracture energy and durability of the silane pretreated joints to be assessed.

EXPERIMENTAL

Preparation of the substrates

The aluminium mirrors were prepared by evaporating aluminium metal (99.99%; Specpure, Johnson-Matthey plc) onto degreased Corning 7059 glass microscope slides. The evaporated aluminium substrates were then cleaned prior to pretreatment with the silanes using an ungettered argon plasma sputter etch. The power used was 566 mW cm^{-2}, the argon gas pressure was 4 mm Hg and the etch time was 5 min. After removal from the pretreatment solution, the cleaned substrates were immediately immersed in the pretreatment solution.

The British Standard (BS) 1200 aluminium substrates were prepared by etching in 1.5 M sodium hydroxide at 50°C for 10 min. The excess alkali was then rinsed off using distilled water before the etch residues were removed by immersing the substrates in 10% nitric acid for 1 min. It should be noted that the nitric acid solution appeared to need some 'conditioning', as high quality monolayers could only be formed after several substrates had been etched in the same solution. This observation may be analogous to the conditioning needed by chromic acid solutions used to etch aluminium substrates. Finally, the excess nitric acid was removed using distilled water. The water completely wetted out the etched aluminium surface, indicating that the surfaces were hydrophilic and suitable for pretreatment using the silanes. In order to minimize the exposure of the cleaned surfaces to the atmosphere and hence contamination, the wet substrates were initially immersed in ethanol to remove the water and then in chloroform. The excess chloroform was then quickly removed using a stream of hot air and was then immediately placed in the pretreatment solution.

Silane pretreatment of the substrates

The pretreatment solution was a 0.1 M solution of the trichlorosilanes in 90% hexadecane/10% chloroform. The methyl terminated trichlorosilanes with chain lengths of six to 20 (Lancaster Synthesis, UK) and were used without any further purification. The vinylic terminated trichlorosilanes 10-undecenyltrichlorosilane and 18-nonadecenyltrichlorosilane were synthesized at Imperial College, using the method summarized in the next section. The solvents used in the pretreatment solutions were purified by using a column of basic alumina (Aldrich Chemical Co. Ltd, UK) to remove the polar impurities. The purified solvents were checked for any polar impurities using the method recommended by Bigalow[19]. This involved placing a droplet of the purified solvent on an aqueous solution of sodium hydroxide (pH > 10). If the radius of the droplet did not increase with time, the solvent was considered to be free of polar impurities. The substrates were pretreated by immersion horizontally in a glass petri dish for 20 min. After pretreatment the substrates were rinsed with chloroform and then distilled water and were finally dried in a stream of hot air.

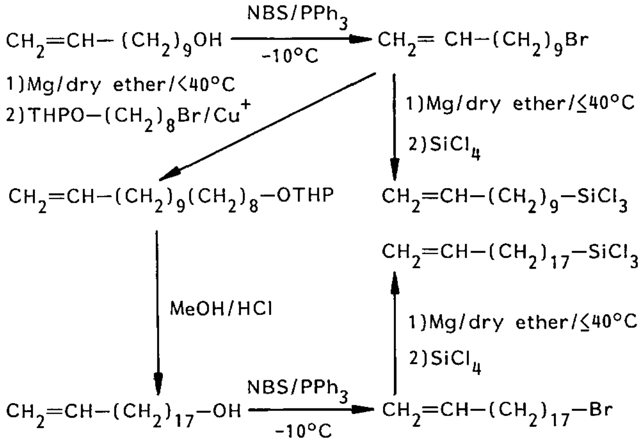

Figure 1 The reaction pathway used to synthesize 10-undecenyltrichlorosilane and 18-nonadecenyltrichlorosilane

Synthesis of the vinylic terminated trichlorosilanes

The reaction pathway used to synthesize the vinylic-terminated trichlorosilanes is summarized in *Figure 1* and is described in detail in Ref. 28. 10-Undecenyl alcohol was reacted with N-bromosuccinamide (NBS) and triphenylphosphine (PPh_3) in dichloromethane at −10°C to yield 10-undecenyl bromide. The bromide was then used to prepare the magnesium Grignard reagent in diethyl ether which was then reacted with silicon tetrachloride in toluene to yield 10-undecenyltrichlorosilane. The pure product was obtained by vacuum distillation at 120°C/0.1 mm Hg using a rotating ball oven.

In order to produce the 18-nonadecenyltrichlorosilane, a carbon to carbon coupling reaction was used. 10-Undecenyl magnesium bromide was prepared as described above, except that the reaction was performed in dry tetrahydrofuran (THF). Lithium cyanochlorocuprate[29] (5 mol%) was added in order to catalyse the reaction. The above solution was cooled to below −5°C and tetrahydropyranyloxy-8-octane bromide in THF was then slowly added ensuring that the temperature did not exceed 0°C. This reaction resulted in the formation of the C19 carbon chain. The protective tetrahydropyranyloxy (THPO) was then simply removed using methanol acidified using 1 M HCl at 50°C. This reaction yielded a solid, 18-nonadecenyl alcohol. The trichlorosilane was then simply synthesized using the same reaction sequence used to produce the 10-undecenyltrichlorosilane. The product was once more obtained using vacuum distillation at 180°C/0.1 mm Hg after a lower boiling fraction was removed at 120–140°C/0.1 mm Hg. The purity of the 18-nonadecenyltrichlorosilane was lower than expected and this was believed to be due to the presence of octane-1,8-ditrichlorosilane. This impurity could not be fully removed from the 18-nonadecenyltrichlorosilane product and was due to incomplete reaction of the tetrahydropyranyloxy-8-octane bromide with the Grignard reagent. The effects of the impurity on the adsorbed 18-nonadecenyltrichlorosilane films is discussed in a later section.

Activation of the terminal vinylic group

The terminal vinylic group was activated to form a hydroxyl group using the method proposed by Netzer *et al.*[25,26]. This process involved immersing the adsorbed vinylic terminated trichlorosilane films into a 1 M solution of diborane in THF (Aldrich Chemical Co., UK) for 2 min. The slides were then removed and then dipped for a further 2 min into a 30% solution of hydrogen peroxide in 0.1 M sodium hydroxide. Upon removal, substrates were rinsed using distilled water and were dried using hot air.

Analysis of the adsorbed silane films

Contact angle studies. The contact angles formed by droplets of water and hexadecane on the adsorbed silane films were measured using the sessile drop method using a Rame–Hart model 100-00 goniometer. The water was double-distilled and the hexadecane was purified using a column of basic alumina to remove all the polar impurities. Each droplet had a volume of 0.02 ml and a total of 20 measurements were conducted on each substrate. The droplets were allowed to stabilize on the surface for 15 s before the angle formed on both sides of the droplets were measured and the mean value recorded. The accuracy of the measurements was typically ±3°.

Ellipsometry studies. The ellipsometry measurements were made using a Rudolf AutoEl ellipsometer at an angle of 70°, employing a 5 mW helium/neon laser at a wavelength of 632.8 nm with a spot diameter of 0.63 mm. The accuracy of these measurements was considered to be ±0.3 nm. As ellipsometry ideally requires a specular, optically flat, highly reflective surface, this technique was only used to measure the thicknesses of the adsorbed silane films on the evaporated aluminium and silicon surfaces. A total of 20 measurements were made on each sample.

Reflection high energy electron diffraction studies. A high energy 40 keV electron beam was directed at a grazing angle of incidence of 4° onto the silane pretreated substrates. The resulting pattern formed by the electrons diffracted by the adsorbed silane films was recorded using a photographic plate. As an electrically conductive, flat substrate was required, this technique was only used to study the silane films adsorbed onto silicon and evaporated aluminium mirrors. The samples were attached to the sample holder using conductive silver paint.

Secondary ion mass spectroscopy. The adsorbed silane films were studied using secondary ion mass spectroscopy (s.i.m.s.) using a 5 keV argon (+ve) ion beam at beam currents of 1 and 10 nA. The data were collected at a step size of 0.2 atomic mass units (a.m.u.). The scan time at each step was 200 ms and the ion beam was rastered over an area of approximately 6 mm^2. Both the positive and negative s.i.m.s. spectra were acquired.

X-ray photoelectron spectroscopy (X.p.s.). The X-ray photoelectron spectroscopy was performed on a 'VG Scientific' ESCALAB spectrometer using AlKα X-rays at 280 W (14 kV, 20 mA) at a pressure of between 10^{-8} and 10^{-9} Torr. An electron take-off angle of 70° and a pass energy of 50 eV were used.

The blister test

In order to prepare the blister test joints after silane pretreatment of the aluminium substrates, 35 g of a polyurethane resin (Solithane 113; Morton-Thiokol) was cast onto the substrates and the adhesive was allowed to cure for 2 days at 30°C before being removed from the mould. The prepared joints were then conditioned at 30°C for 2 weeks before being tested.

In order to determine the initial adhesive fracture energy, G_c, the cured joints were tested using the blister test using dry nitrogen as the pressurizing medium. The equipment used has been recently described in detail by Fernando and Kinloch[30]. A constant nitrogen gas flow of 10 cm^3 min^{-1} was used throughout this part of the work. The failure pressure at a range of blister radii was recorded and the adhesive fracture energy, G_c, was calculated using equations (2) and (3) developed by Andrews and Stevenson[31].

$$P_c^2 a = E \cdot G_c \cdot f(h/a) \qquad (2)$$

where P_c is the critical failure pressure, G_c is the adhesive fracture energy, E is the Young's modulus, h is the thickness of the polymer and a is the blister radius. The term $f(h/a)$ is a geometry factor and may be expressed by:

$$f(h/a) = [1/(1-\nu^2)] \times \{3/32[(a/h)^3 + 4/(1-\nu)\cdot(a/h)] + 2/\pi\}^{-1} \qquad (3)$$

The thickness of the polyurethane adhesive was 17 mm, the Young's modulus of the polymer was 3.38×10^6 N m^{-2} and the Poisson's ratio was assumed to be 0.49. The pressure was raised until the blister radius increased and the pressure was recorded. After the blister radius increased, the pressure was then briefly raised to a much higher pressure than that required to cause blister growth. This caused rapid crack propagation and the pressure was then rapidly reduced to atmospheric pressure. This procedure ensured that the crack tip remained sharp. The new blister radius was then measured and the test repeated. A total of three joints were studied using the above procedure and typically five measurements were obtained from each joint.

The durability of the joints was obtained by pressurizing the joints to 50% of their failure pressure for a given initial blister radius (typically 8 mm) using water and then monitoring the time for the onset of crack propagation to occur. The time required for the joints to completely fail was also recorded. In order to assess the effect of the silane pretreatments, unpretreated aluminium joints were also studied. A total of three joints were tested for each trichlorosilane. To identify the locus of failure of the joints, 1 cm^2 samples were cut from the failed joints and the polymer and metal fracture surfaces were analysed using X.p.s.

RESULTS AND DISCUSSION

Methyl-terminated trichlorosilane films

Contact and ellipsometry studies. The contact angle results obtained from the BS 1200 aluminium alloy substrates pretreated using methyl terminated trichlorosilanes with chain lengths of between 6 and 20 are presented in *Figure 2*. The increase in the hexadecane and water contact angle results observed for chain lengths of between 12 and 16 implies that the surface energy of the adsorbed films has reduced. Shafrin and Zisman have shown that methyl groups possess a lower surface energy then methylene groups[32]. Thus the results presented in

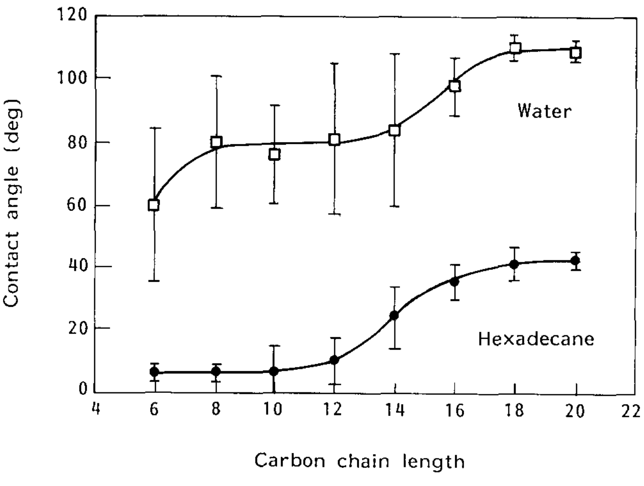

Figure 2 Variation in water and hexadecane contact angles with the chain length of long-chained methyl-terminated trichlorosilanes adsorbed onto BS 1200 aluminium alloy substrates

Table 1 Contact angle and ellipsometry results obtained from decyl (DTS) and octadecyltrichlorosilane (OTS) films adsorbed onto aluminium substrates

Substrate	Silane	Contact angles (deg) Water	Contact angles (deg) Hexadecane	Depth (nm)
Al mirror	OTS	112	42	3.1
Al mirror	DTS	94	10	1.5
Al alloy	OTS	112	41	–
Al alloy	DTS	78	8	–

Figure 3 Electron diffraction pattern obtained from a decyltrichlorosilane film adsorbed onto aluminium mirrors

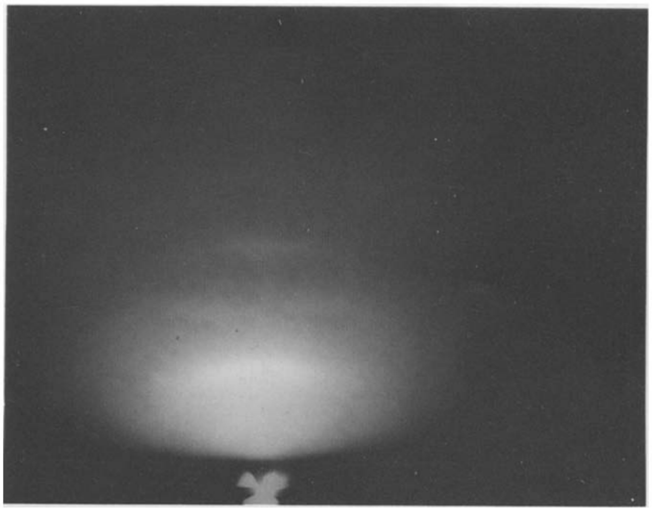

Figure 4 Electron diffraction pattern obtained from an octadecyltrichlorosilane film adsorbed onto aluminium mirrors

Figure 2 indicate that the surface of the adsorbed films is changing from being methylene to being predominantly methyl in character as the chain length increases. Similar results have been previously obtained by a number of workers[19–21,23–25]. The results presented in *Figure 2* clearly indicate that high quality films can be deposited onto surfaces with degrees of roughnesses typically used in adhesive bonding applications.

In order to determine whether the trichlorosilanes adsorbed to form monolayer films, decyl (DTS) and octadecyltrichlorosilane (OTS) were adsorbed onto aluminium mirrors and the resulting films were studied using both contact angle measurements and ellipsometry. These results are presented in *Table 1*. The contact angle results are similar to those obtained from the BS 1200 aluminium substrates presented in *Figure 2* for the DTS and OTS films. The ellipsometry results obtained from the OTS films show that the films' thicknesses were approximately 3.0 mm, similar to the length of a fully extended OTS molecule (approximately 2.9 nm). The DTS films exhibited more variation, but an average film thickness of 1.5 nm was obtained, which is slightly lower than that expected for a fully extended DTS molecule (1.8 nm). The contact angle and ellipsometry data indicate that these long-chained trichlorosilanes adsorbed to form monolayer films. Once more this result is in agreement with the previously published work[20,21,23–25].

R.h.e.e.d. studies. In order to gain some information regarding the orientation of the silane molecules on the surface, the DTS and OTS films adsorbed onto the aluminium mirrors were studied using reflection high energy electron diffraction (r.h.e.e.d.). The diffraction patterns obtained from the DTS and OTS films are presented in *Figures 3* and *4* respectively. The diffraction pattern from the DTS film consists of a single broad curved band, whereas the pattern from the OTS film contains some diffuse diffraction spots. The presence of these diffraction spots indicates that the OTS films possess a degree of orientation, whereas the DTS films do not. The above patterns cannot be attributed to the aluminium surface since examination of the clean aluminium surface revealed that at the aluminium surface was polycrystalline and so diffraction rings were observed. In addition, after plasma cleaning the aluminium mirrors, no diffraction pattern was obtained, which indicates that the aluminium surface was then amorphous. Therefore, the observed patterns are due to the adsorbed trichlorosilane filmes.

Similar diffraction patterns have been previously obtained by Mentor and Tabor from long-chained molecules adsorbed onto various substrates[27]. These workers concluded that the appearance of the maxima and minima in the diffraction patterns indicated that the hydrocarbon chains were orientated away from the substrate. Therefore, it appears that the hydrocarbon chains in the OTS films adsorbed onto the aluminium substrates are also orientated away from the substrate. This conclusion also is consistent with the contact angle results, since for the surface to consist of densely packed methyl groups, the hydrocarbon chains must also pack together, which implies that the chains orient themselves in a common direction.

Mentor and Tabor also found that when adsorbed orientated monolayer films were heated, the r.h.e.e.d. diffraction spots coalesced to form a line. Upon continued heating, the line curved and the resulting diffraction pattern then resembled the patterns obtained from the unorientated DTS films (see *Figure 3*). Upon continued heating, the r.h.e.e.d. patterns completely disappeared, but the original patterns reappeared upon cooling. These results suggest that the ability of the longer chained films to orientate is partly due to increased van der Waal's forces being able to overcome the disorientating effects of temperature. In addition to chain length, the disorientation effect also strongly depended on the substrate.

Table 2 X.p.s. results obtained from aluminium surfaces with decyl (DTS) and octadecyltrichlorosilane (OTS)

Substrate	Silane	Carbon (%)	Silicon (%)
Al mirror	OTS	36	1.9
Al mirror	DTS	32	2.7
Al alloy	OTS	35	2.0
Al alloy	DTS	22	1.2

For example, the adsorbed films of octadecanoic acid (possessing a chain length of 18) on copper, the disorientation temperature was 80°C, whereas on nickel, it was 100°C. As Porter *et al.*[33] have pointed out, the orientation of the films depends on the difference between the size of the head groups and the tail and also on the difference between the head group and the adsorption sites on the substrate. The greater the differences between these parameters at a particular temperature, the longer the hydrocarbon chain must be before the chains can pack densely together. An example of an optimum situation is the adsorption of thiols onto the gold. Bain and Whitesides[24] found that highly orientated monolayers were obtained using thiols with a chain length of only 11. In the current work and also the work of Netzer *et al.*[25,26], the much larger trichlorosilane head group means that a chain length of 18 was required to form orientated monolayers on aluminium. However, during this work, it was also found that orientated trichlorosilanes with chain lengths of only 12 atoms formed high quality monolayers on glass. Thus, the substrate, the type of head group and the chain length can all play a role in determining the structure of an adsorbed film at a particular temperature.

X.p.s. and s.i.m.s. studies. The adsorbed DTS and OTS film on both alkaline etched BS 1200 aluminium alloy and aluminium mirrors were also studied using both X.p.s. and s.i.m.s. The X.p.s. results are summarized in *Table 2*. For the OTS films, both the carbon and silicon results on both substrates are very similar. These results indicate that similar films were formed on both substrates, and therefore support the contact angle results. In the case of the DTS films, on the BS 1200 aluminium alloy, the silicon and carbon intensities are lower than those obtained from the OTS films. This is expected as the contact angle and r.h.e.e.d. results, discussed above, have shown that the DTS films are less tightly packed than the OTS films. The reduction in the carbon intensities reflect both the reduction in the packing density of these films and also the shorter chain length of the DTS molecule. On the aluminium mirror pretreated with DTS the silicon level was significantly higher than that obtained from the adsorbed OTS films. This is unexpected, as the silicon levels should be lower to reflect the lower packing density of the adsorbed DTS films compared to the adsorbed OTS films. However, silicon was detected using X.p.s. from a plasma-etched, unpretreated aluminium mirror and so some contamination of the DTS sample by an air-borne silicon-containing compound may have occurred. The similarity between the X.p.s. results from the aluminium mirrors and the BS 1200 aluminium alloy substrates pretreated using OTS, indicates that contamiination did not occur on the OTS-pretreated aluminium mirror. It should be noted that the aluminium mirrors were prepared, plasma etched and silane pretreated in a separate laboratory from the BS 1200 aluminium alloy substrates.

The s.i.m.s. spectra from octadecyl and decyltrichlorosilane films adsorbed onto plasma-etched aluminium mirrors and BS 1200 aluminium alloy substrates were obtained in an attempt to determine the trichlorosilane/aluminium interaction. All the spectra were very similar and so only the spectra obtained from octadecyltrichlorosilane adsorbed onto aluminium mirrors are presented in *Figure 5*. The positive s.i.m.s. spectra (*Figure 5a*) exhibit a series of peak groups gradually decreasing in intensity with increasing mass. The separation of the peak groups is approximately 14 and so the spectrum is due to the fragmentation of the hydrocarbon chains. The peak with an atomic mass unit (a.m.u.) of 71 could be assigned to $[\mathrm{Al{-}O{-}Si}]^+$, but a carbon chain fragment with the structure $[C_5H_{11}]^+$ would also possess a mass of 71. In the negative s.i.m.s. spectra, the most interesting peaks were detected at 103 and 119 a.m.u. (*Figure 5b*). These could be assigned to the species $[AlO_3Si]^-$ and $[AlO_4Si]^-$, which would indicate the existence of Al–O–Si bonds. The detection of these peaks would be analogous to the detection of $[FeO_3Si]^-$ and $[FeO_4Si]^-$ species by Cayless and Perry[9] from a silane-pretreated iron surface. However, silicon and aluminium possess atomic masses separated by only one. Thus, the peaks at 103 and 119 could also be due to $[Al_2O_3H]^+$ and $[Al_2O_4H]^+$. Thus, once more tha s.i.m.s. results cannot be used to identify the silane/aluminium interaction. However, the fact that no peaks due to $[\mathrm{Si{-}O}]^-$ (a.m.u. 44) or $[\mathrm{Si{-}O_2}]^-$ (a.m.u. 60) were detected is interesting, since these peaks, assigned to the presence of a poly-

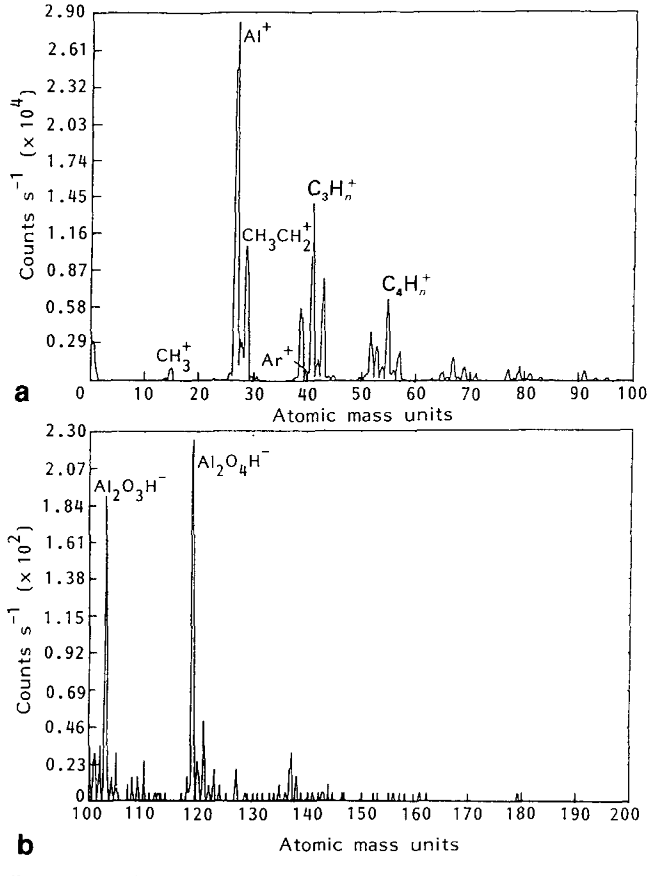

Figure 5 Positive (a) and negative (b) s.i.m.s. spectra obtained from an adsorbed octadecyltrichlorosilane film on aluminium mirrors

Table 3 Contact angle and X.p.s. results obtained from unactivated, activated and isocyanate-capped 10-undecenyl (UTS) and 18-nonadecenyltrichlorosilane (NTS) films on BS 1200 alloy aluminium substrates

		Contact angles (deg)		X.p.s. analysis (%)		
Silane	Terminal group	Water	Hexadecane	C	N	Si
UTS	C=C	77	Wetted	22.5	0.8	1.6
UTS	OH	55	Wetted	20.5	0.6	2.1
UTS	-N=C=O	73	Wetted	21.7	1.4	1.6
NTS	C=C	85	25	29.8	0.8	2.6
NTS	OH	52	Wetted	25.0	0.4	1.5
NTS	-N=C=O	73	Wetted	27.6	1.6	1.4

siloxane, were detected by Cayless and Perry. Therefore, from the s.i.m.s. studies, it appears that these long-chained trichlorosilanes did not absorb to form a polysiloxane network and no definitive evidence supporting the formation of interfacial covalent bonds was obtained.

Recent work by Cave *et al.*[34] measured the silicon Auger parameter using high energy X.p.s. The silicon aluminium was found to be 3453.0 eV, whereas the Auger parameter from fully hydrolysed, thick trichlorosilane film (i.e. containing Si–O–Si bonds) was 3452.0 eV. The difference was attributed to the less electronegative aluminium atom allowing the silicon in an Al–O–Si bond to retain an increased level of electron density, thus increasing the silicon Auger parameter. Thus, this result suggests that Al–O–Si bonds were indeed formed. This observation is in agreement with the studies performed by Naviroj *et al.*[10], who examined the adsorption of an aminosilane onto alumina powder using diffuse reflection i.r., and also concluded that interfacial Al–O–Si bonds can be formed. In addition, the work of Cave *et al.* detected no silicon component with an Auger parameter of 3452.0 eV from the monolayer OTS pretreated aluminium substrates. This additional result therefore supports the s.i.m.s. results in that very little or no polysiloxane formation occurred.

Vinylic-terminated trichlorosilane films

Adsorbed films of the vinylic-terminated 10-undecenyltrichlorosilane (UTS) and 18-nonadecenyltrichlorosilane (NTS) were studied using both contact angles and X.p.s. and these results are presented in *Table 3*. The contact angle results from the unactivated UTS film are similar to those obtained from the DTS film on BS 1200 aluminium alloy. After activation, to form terminal hydroxyl groups, there was a clear decrease in the contact angles, which indicates that the vinylic groups were indeed converted to hydroxyl groups. In order to determine if these hydroxyl groups were available for reaction with isocyanate groups, the activated films were immersed in butyl isocyanate. The contact angles increased and the X.p.s. nitrogen levels also increased slightly, indicating that the terminal hydroxyl groups had reacted. Some variation in the silicon levels was detected, but no significant increase in the carbon levels could be associated with the higher silicon levels. Thus, the reason for the variation in the UTS films is not known.

In the case of the NTS films, the contact angle and X.p.s. results once more confirm that NTS films adsorbed to form monolayer films and that the vinylic groups could be activated and could read with an isocyanate. However, while the contact angles were higher than those obtained for the UTS films, the angles were nevertheless much lower than those obtained from the OTS films. The reason for this was traced to the presence of an impurity, believed to be octane-1,8-ditrichlorosilane, formed during the synthesis of the NTS. This impurity could not be completely removed by distillation. The effect of simultaneously co-adsorbing two molecules with differing chain lengths has been elegantly investigated by Bain and Whitesides[24]. These workers adsorbed two hydroxy-terminated thiols with chain lengths of 11 and 19 onto gold substrates and investigated the adsorbed films using contact angle measurements and ellipsometry. Their results showed that for the pure compounds the films consisted of fully orientated monolayer films. As the proportion of the short-chained thiol was increased, the films became progressively more disordered, but it was only when the levels of the short-chained molecule approached 50% that the contact angle and ellipsometry results indicated that the adsorbed films were becoming disordered. These results therefore indicated that the longer-chained molecules were able to overcome the disorientating effects of the shorter chained molecule. These results would therefore suggest that a similar effect is occurring in the case of the NTS films, namely, the disilane impurity has prevented the NTS molecules from forming films as densely packed as the OTS films discussed above. The impurity levels causing the disorientation effects in the current research were approximately 15% which is much lower than the 50% levels observed by Bain and Whitesides. However, as the impurity in this work possessed two head groups and therefore both head groups would probably adsorb onto the aluminium substrate, the disorientation effect would be expected to be more pronounced than that observed by Bain and Whitesides.

Mechanical testing

Adhesive fracture energy studies. The adhesive fracture energy (G_c) results obtained using the blister test are summarized in *Table 4* and the results are also presented in *Figure 6*. The data shown in *Figure 6* clearly reveal that the experimental results follow the relations given in equations (2) and (3) and that the value of G_c is independent of the blister diameter.

These results clearly show that the activated vinylic terminated trichlorosilanes possess a relatively high adhesive fracture energy. Recent work by Cave and Kinloch[35] showed that similar aluminium joints pretreated using 3-aminopropyltrichlorosilane possessed an adhesive fracture energy of approximately 14 J m^{-2}. Thus the activated long-chained trichlorosilanes have

Table 4 Adhesive fracture energies and durabilities obtained using the blister test from BS 1200 aluminium alloy/polyurethane joints pretreated with long-chained trichlorosilanes

			Durability results	
Silane	Terminal groups	G_c (J m^{-2})	Applied G_c (J m^{-2})	Time to failure (s)
None	–	6.9	3.5	360
OTS	Methyl	1.6	Not performed	
UTS	Hydroxyl	18.1	9.1	<60
NTS	Hydroxyl	18.2	9.1	540

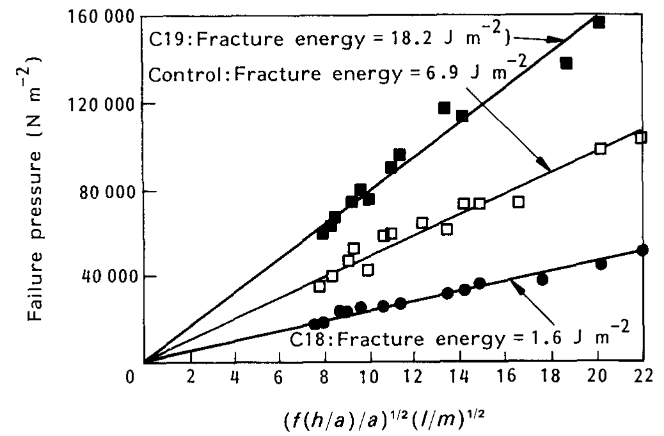

Figure 6 Plot of the critical failure pressure *versus* the corrected blister test for unpretreated BS 1200 aluminium alloy joints and joints pretreated using octadecyltrichlorosilane and activated 18-nonadecenyltrichlorosilane

yielded a valuable increase in the adhesive fracture energy compared to the commercial silanes currently available.

The very low fracture energy of the OTS film (methyl terminal group) is also interesting as it is much lower than the fracture energy obtained from the unpretreated control joint. X.p.s. analysis of the fracture surfaces indicated that the locus of failure occurred at the silane/polymer interface, therefore OTS may have applications in the field of *abhesive* coatings and release agents. X.p.s. analysis of the metal fracture surfaces from the UTS pretreated joints detected very low silicon levels (0.3%). From the results presented in *Table 4*, a silicon level of approximately 1.6–2.0% would be expected. The very low silicon levels therefore imply that the bonds between the silane head group and aluminium oxide surface were broken. In the NTS films, as the same fracture energy was obtained, very low silicon levels would have been expected to be detected on the aluminium surface. However, some silicon was detected on the metal failure surface (0.9%), but at much lower levels than that detailed in *Table 3*. This most probably arose from the disilane impurity.

Durability studies. The durability results were obtained by applying 50% of the adhesive fracture energy using water as the pressurizing medium and are presented in *Table 4*. The durability of the adsorbed UTS films is extremely poor with the onset of crack propagation occurring within 60 s. However, the NTS films are considerably better, with 540 s being required before crack propagation was observed. This is considerably better than the durability of the unpretreated control joints, especially when the much higher applied load used to test the silane pretreated joints is also considered. The locus of failure determined using X.p.s. was once more along the silane/substrate interface. For comparison, the best durability obtained by Cave and Kinloch[35] for aluminium joints pretreated with 3-aminopropyltrimethoxy silane (5 min; pH 6.8) was 1080 s. This value was, however, achieved using a lower applied fracture energy of 7.0 J m^{-2}.

Mechanisms of environmental attack. The reason for the much better durability of the joints pretreated with NTS *versus* those pretreated with UTS is believed to be associated with the increased packing of the longer carbon-chained NTS films compared to the UTS films. This suggestion arises from several observations. Firstly, the results obtained by Cave *et al.*[34] showed that the silicon Auger parameters from aluminium substrates pretreated with UTS and NTS were the same, indicating that the interaction between the silane head group and the aluminium substrates was also the same. Thus, the differences in the durabilities of the UTS and NTS pretreated aluminium joints cannot be explained in terms of changes in the interfacial interactions between the silane head groups and the aluminium oxide surface. Secondly, the work summarized in the section on methyl-terminated trichlorosilane films showed that the differences in structure between the adsorbed UTS and NTS films was due to differences in chain orientation. These differences arose from the improvement in the packing of the hydrocarbon chains for the longer-chained NTS films compared to the UTS films. Turning to the durability experiments, in the NTS films the closer packing of the hydrocarbon chains would be expected to impede the diffusion of water towards the interface. In the UTS films the disorientated nature of the films would allow the water to diffuse rapidly through the film to the interface, where it would rapidly be able to break the interfacial bond between the silane and the aluminium surface.

Another point of interest concerns the use of monolayer silane films as adhesion promoters with heat-cured adhesives. The r.h.e.e.d. work by Mentor and Tabor[27] showed that orientated monolayer films could be thermally disorientated. These researchers also showed that the films reorientated themselves upon cooling. However, if these films were used as adhesion promoters with an adhesive that cured above the disorientation temperature of the adsorbed film, the activated end-group would react with the adhesive resin, possibly preventing the film from reorientating itself upon cooling. The adsorbed silane film after curing of the adhesive would therefore be similar in nature to the UTS films studied above. Therefore, from the results discussed above, these joints would not be expected to yield durable adhesive joints. However, Mentor and Tabor found that the disorientation temperature for the same substrate/head group interaction increased with increasing chain length. For example octadecanoic acid (with a chain length of 18) adsorbed onto mild steel disorientated at 95°C, whereas octacosanoic acid (with a chain length of 28) disorientated at 125°C. Thus, the possibility exists that by choosing the correct chain length, the disorientating effects of temperature could be overcome. This would allow these long-chained vinylic-terminated silanes to be used as adhesion promoters with heat-cured adhesives.

Finally, one problem which currently hinders the application of these silanes as adhesion promoters is the activation procedure used to convert the terminal vinylic group to a hydroxyl group. The activation procedure involves the use of diborane, which is both toxic and also releases hydrogen upon contact with moisture. Thus, a safer activation procedure is clearly required. The presence of the terminal vinylic group does, however, allow direct reaction with adhesives that cure via a free radical mechanism such as acrylics-based adhesives.

CONCLUSIONS

The work described above has clearly shown that long-chainged trichlorosilanes adsorb to form monolayer films. When the chain length equals or exceeds 18, the hydrocarbon chains pack tightly together and they orientate themselves away from the substrate. When vinylic-terminated trichlorosilanes were investigated, it was found that the vinylic groups could be easily converted into hydroxyl groups and that these groups were available for reaction with isocyanate-cured adhesives.

The work performed using the blister test showed that these activated monolayer silane films are capable of acting as adhesion promoters. These silanes yield higher adhesive fracture energies under dry conditions than can be obtained using the commercial silanes currently available. In order to obtain good durability it is necessary for the silane to possess a chain length of at least 18. The dense packing of the chains appears to impede the diffusion of water to the silane/aluminium interface. However, in this work, the presence of a short-chained impurity prevented the ultimate durability performance of these silanes from being assessed. A high quality monolayer silane film may therefore allow the durability of adhesive joints to be further improved. Nevertheless, the films studied appeared comparable to the best performance achieved using a commercially available silane.

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