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A. J. Kinloch^a; K. T. Tan^a; J. F. Watts^b

^a Department of Mechanical Engineering, Imperial College London, London, UK ^b Surface Analysis Laboratory, School of Engineering, University of Surrey, Guildford, Surrey, UK

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Novel Self-Assembling Silane for Adhesive and Adhesive Applications

A. J. Kinloch

K. T. Tan

Department of Mechanical Engineering, Imperial College London,
London, UK

J. F. Watts

Surface Analysis Laboratory, School of Engineering, University of
Surrey, Guildford, Surrey, UK

The potential benefits from using a novel vinyl-terminated long alkyl-chain self-assembling silane (VTS) have been investigated. A relatively high water contact angle of 83° was found for water on the VTS-pretreated soda-lime glass surface. This revealed that the degree of hydrophobicity of this surface was far more pronounced than for the ultrasonically-cleaned glass surface or the γ -glycidoxypropyl-trimethoxy silane (GPS)-pretreated glass surface, which gave contact angles of 14° and 42°, respectively. Further, good agreement between the measured and the theoretical contact angles for a fully adsorbed vinyl-terminated self-assembled monolayer surface implied that the VTS molecules were adsorbed with the vinyl-terminal groups orientated away from the glass surface. Indeed, X-ray photoelectron spectroscopy (XPS) analysis confirmed that the VTS molecules were adsorbed as a monolayer with the vinyl-terminal groups orientated away from the glass surface. Double-cantilever beam joints were prepared using these various pretreated-glass substrates, using an epoxy adhesive, and they were tested employing a fracture-mechanics approach. The adhesive fracture energy, G_C , of the VTS-pretreated glass/epoxy joints was found to be far lower in value than for the ultrasonically cleaned joints or the GPS-pretreated joints. The potential applications of this novel long alkyl-chain silane are twofold: (a) the relatively very poor adhesion of the VTS pretreatment enables this silane to be used as an excellent adhesive layer, i.e., as a release agent, and (b) the presence of reactive vinyl-terminal groups might allow this silane to be activated to form functional groups that may then react with an adhesive, such as an epoxy resin, and so act as an excellent adhesion promoter to increase the durability of the adhesive joint.

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Address correspondence to A. J. Kinloch, Department of Mechanical Engineering, Imperial College London, Exhibition Road, London, SW7 2BX, UK. E-mail: a.kinloch@imperial.ac.uk

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1. INTRODUCTION

Commercially available short alkyl-chain silane primers have been used extensively to decrease the susceptibility of the adhesive-substrate interface to attack by water; see for example Refs. [1–3]. The ability of these silanes to promote enhanced adhesion to metallic and ceramic substrates is a result of the specific interaction, *via* a condensation reaction, between the silanols of the hydrolysed silane with hydroxyl groups present on the surface of the substrate to form covalent bonds [1,2]. Typically, there is also a functional terminal group at the other end of the silane molecule, which may react with the adhesive. Thus, silanes may couple, *via* covalent bonding, the substrate to the adhesive.

However, such commercially available silane primers have a relatively short alkylchain in their chemical structure and typically adsorb onto the surface of the substrate as disordered multilayers. For example, γ -glycidoxypropyltrimethoxysilane (GPS) typically adsorbs with approximately 50% of the silanol groups pointing upward and 50% pointing downward [4] and typically forms a multilayer polysiloxane structure consisting of between 5 and 25 molecular layers [5]. Thus, although these multilayer silane primers may indeed form strong covalent bonds across the adhesive/substrate interface, the presence of a relatively thick and weak polysiloxane layer (a) may lead to a cohesive failure in the polysiloxane and (b) still leads to water being able to permeate through the polysiloxane and so reach the silane/substrate interface, where it may disrupt even primary interfacial bonding [6]. Therefore, the silane performance might be significantly improved if the silane could be adsorbed as a highly ordered monolayer film: indeed, for example, in the manner of a self-assembled monolayer (SAM), in such a way that the alkyl chains are densely packed together and orientated, so making any reactive terminal groups available for reaction with an adhesive. Consequently, this would result in the formation of a covalently bonded bridge between the substrate and the adhesive, but now without the presence of a relatively thick layer of polysiloxane. Also, in a long alkyl-chained silane, the intermediate alkyl chains would be highly hydrophobic, as well as relatively close packed. Therefore, an ordered monolayer film would impede water diffusing through such a SAM-silane layer to the

silane/substrate interface. All of these features should help to impart excellent joint durability.

To enable silane molecules to form a monolayer film and self-assemble on substrates in such a way that the alkyl chains will be densely packed together and be orientated away from the substrates, it has been demonstrated [7,8] that a critical minimum alkyl chain length of about 18 and a particular substrate-head group combination are required. The objective of the present research was to explore the potential benefits of using such a SAM silane. A novel vinyl-terminated long alkyl-chain self-assembling silane, with 20 alkyl groups in the chain, was studied. Contact-angle measurements and X-ray photoelectron spectroscopy (XPS) have been undertaken to investigate the details of the silane adsorption. In addition, linear-elastic fracture-mechanics tests have been conducted using adhesively bonded double-cantilever beam (DCB) specimens to assess the toughness and durability of the silane-pretreated joints.

2. EXPERIMENTAL

2.1. Materials

The novel long alkyl-chain silane investigated was 22-triethoxysilyldocos-1-enesilane, *i.e.*, a vinyl-terminated long alkylchain silane (VTS). A γ -glycidoxypropyltrimethoxysilane (GPS) was also investigated for comparative purposes. The schematic chemical structures of the two silanes are shown in Figure 1. The VTS was synthesized by Target Molecules Ltd. (Southampton, UK), whilst the GPS was supplied by OSI Specialities (Wilton, CT, USA). The adhesive used was a

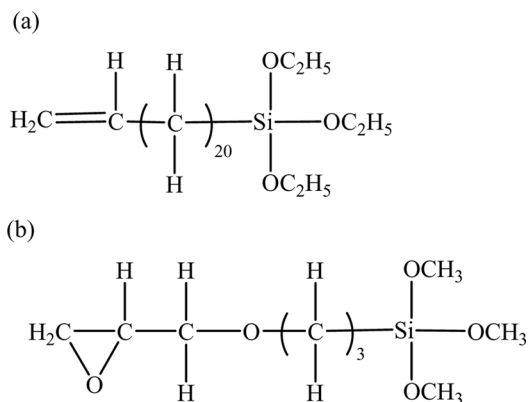


FIGURE 1 Structures of (a) the VTS and (b) the GPS.

TABLE 1 Bulk Composition of the Toughened Soda–Lime Glass

Materials	Chemical formula	Composition (%)
Sand	SiO ₂	72.8
Soda ash	Na ₂ O	13.0
Limestone	CaO	8.4
Dolomite	MgO	4.0
Alumina	Al ₂ O ₃	1.0
Other	—	0.8

hot-curing rubber-toughened epoxy adhesive, which was based upon a dicyandiamide-cured diglycidyl ether of bisphenol-A. The product grade for this adhesive was XD[®] 4236-2, from Huntsman Advanced Materials (Duxford, UK). The substrates used throughout the present work were manufactured from toughened soda–lime glass. (Glass substrates were used to adsorb the long alkyl-chain silane, because the glass surfaces are relatively smooth, which should assist the silane to self-assemble and thereby form an ordered monolayer film.) The bulk composition of the glass is given in Table 1.

2.2. Specimen Preparation

The adhesively bonded DCB test geometry was employed and is schematically illustrated in Figure 2. The silane solution consisted of 1% w/w of silane and 99% w/w of solvent, which was a mixture of 90% w/w ethanol and 10% w/w deionised water. The solution was stirred continuously for 1 h to allow the silane to hydrolyse. Meanwhile, the glass substrates were first cleaned with acetone to remove gross contamination before being cleaned ultrasonically in a bath of deionised water. In the case of the silane-pretreated substrates, immediately after the silane solution was ready, the glass substrates were dipped into the solution for 10 s. The substrates were then rinsed with the solvent used to prepare the silane solution. The silane-pretreated glass substrates were then dried at 93°C for 1 h and allowed to cool to room temperature, before being bonded to form the DCB joint. Prior to joint preparation, a thin layer of polytetrafluoroethylene film was laid onto one of the glass substrates to create a starter crack. Typically, this extended about 40 mm from the loading end. Meanwhile, the adhesive was degassed in a vacuum oven at 80°C before being applied to the substrates. The bond-line thickness of the adhesive was controlled during manufacture using 0.5-mm-diameter wire inserts. Finally, the joints were held in a purposed-built jig and the adhesive was cured at 130°C for 3 h.

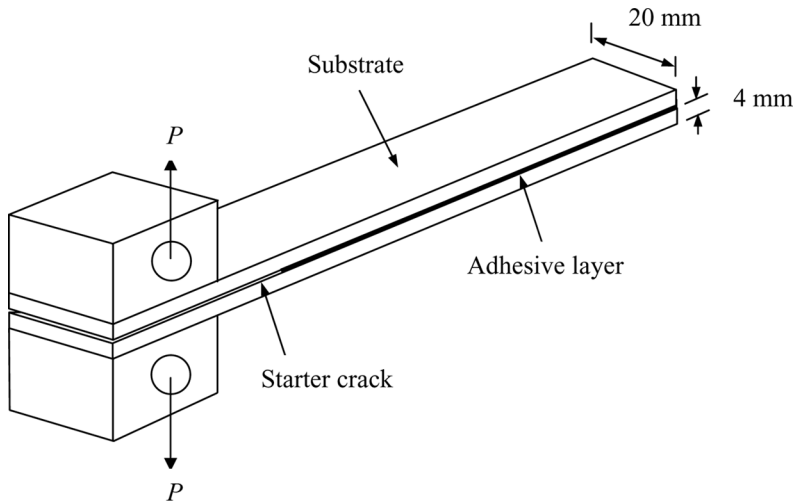


FIGURE 2 DCB adhesive joint. The thickness of the adhesive layer was 0.5 mm, and the length of the substrate beam was 140 mm.

2.3. Material Characterisation

2.3.1. Contact Angle Measurement

Contact angles formed by droplets of deionised water were measured on the various pretreated glass substrates using the sessile drop method, employing a Ramè-Hart (Netcong, NJ, USA) 100-00 goniometer.

2.3.2. X-Ray Photoelectron Spectroscopy

XPS analyses were undertaken using a Thermo VG Scientific (East Grinstead, UK) Sigma Probe spectrometer. The X-ray source used was monochromatic aluminium $K\alpha$ set to a spot size of $500\ \mu\text{m}$. Survey spectra were performed with a pass energy of 150 eV to detect all peaks, which was followed by a high-resolution examination using a pass energy of 50 eV.

2.3.3. Fracture-Mechanics Tests

The DCB joints were tested under monotonic-loading conditions using a screw-driven Instron tensile-testing machine, in compliance with the relevant test standard, BS 7991 [9]. The tests were conducted at a displacement rate of the cross-head of the Instron (High Wycombe, UK) machine of $10\ \mu\text{m}/\text{min}$. The test environment was

water at $21 \pm 1^\circ\text{C}$. The value of G_C was ascertained from the following equation:

$$G_C = \frac{3Pu}{2B(a + |\Delta|)} \cdot \frac{F}{J}, \quad (1)$$

where P is the critical load, B is the width of specimen, a is the crack length, J is a load-block correction, F is a large displacement correction, u is the displacement, and Δ is a crack-length correction for a beam that is not perfectly built-in [9].

3. RESULTS AND DISCUSSION

3.1. Contact Angle Measurements

The contact angle of water on the VTS-pretreated surface is shown in Figure 3. As described previously, for comparative purposes, two different surface pretreatments, *i.e.*, an ultrasonic-cleaning and a GPS pretreatment, were also investigated. It is noteworthy that the contact angle for the ultrasonically cleaned glass was $14^\circ \pm 3^\circ$ and was the lowest amongst all the surfaces. This is attributed to the fact that the glass surface is of a highly polar nature, and therefore water molecules are able to readily wet the ultrasonically cleaned surface. (However, it should be noted that the contact angle was not zero. We suggest that this is due to relatively low concentrations of adventitious hydrocarbon contamination, which adsorbs onto the cleaned glass surface, either from the wash solutions employed or from the atmosphere after cleaning. This suggestion is confirmed by the results from the XPS studies, as shown and discussed later.)

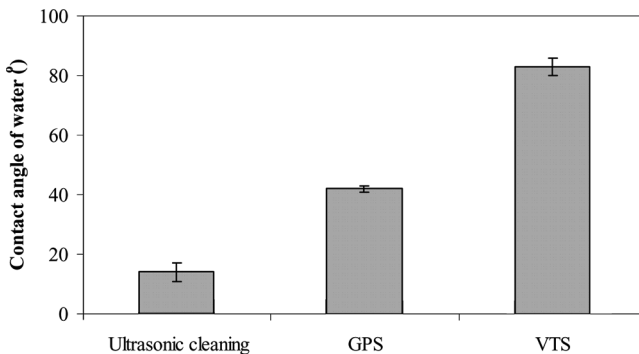


FIGURE 3 Contact angles of water on the various pretreated glass substrates. The error bars represent the standard deviations.

After the adsorption of the GPS film, the contact angle of water on the surface increased significantly and was $42^\circ \pm 1^\circ$, indicating that the nature of the surface was now more hydrophobic than the ultrasonically cleaned surface. Such an increase in the contact angle by nearly a factor of four is due, of course, to the presence of hydrophobic organic functional groups on the GPS-pretreated glass surface.

Turning to the VTS-pretreated glass, as can be seen from Figure 3, the extent of the hydrophobic nature of the VTS-pretreated surface was much more pronounced than for the GPS-pretreated and the ultrasonically cleaned glass surfaces, with a very high contact angle of $83^\circ \pm 3^\circ$. Now, the theoretical contact angle for a SAM silane surface, with the vinyl-terminated orientated away for the glass surface, may be estimated using the Young–Dupré equation:

$$W_a = \gamma_{lv}(1 + \cos \theta), \quad (2)$$

where W_a is the thermodynamically reversible work of adhesion, θ is the contact angle, and γ_{lv} is the surface energy of water. For solely dispersion-force interactions, the relationship between the value of W_a and the surface energies of water, γ_{lv} , and a solid surface, γ_{sv} , may be determined *via* a geometric mean approach as

$$W_a = 2\sqrt{\gamma_{lv}\gamma_{sv}}. \quad (3)$$

Combining Equations (2) and (3) yields

$$\cos \theta = 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} - 1. \quad (4)$$

The values of γ_{lv} and γ_{sv} for water and a fully adsorbed vinyl-terminated SAM surface have been reported to be 72 mJ/m^2 and 26 mJ/m^2 [10], respectively. These values yield a theoretical contact angle for a fully adsorbed vinyl-terminated SAM surface of 78° . This value is clearly in good agreement with the measured contact angle of $83^\circ \pm 3^\circ$. Therefore, it is evident that for the VTS-pretreated glass surface that all, or least a large majority, of the vinyl-terminal groups were orientated away from the glass surface.

3.2. X-ray Photoelectron Spectroscopy Studies

XPS has been employed to determine the elemental compositions of the ultrasonically cleaned and the silane-pretreated glass surfaces. The XPS survey spectra and the elemental composition are shown in Figures 4–6 and Table 2, respectively.

Upon examining the results for the ultrasonically cleaned surface (see Figure 4 and Table 2), it can be seen that silicon and oxygen were

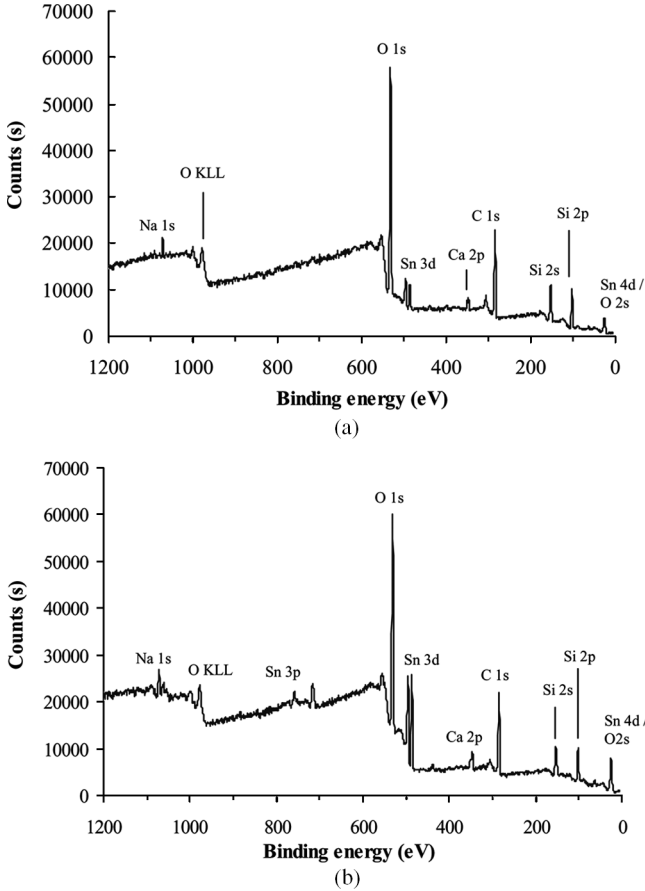


FIGURE 4 XPS survey spectra of the ultrasonically cleaned samples for (a) side 1 and (b) side 2.

detected at relatively high intensities. The detection of a high intensity of oxygen is to be expected, as it is a major component of the soda–lime glass. Sodium and calcium at relatively low intensities were also detected. These elements are also the main chemical constituents of the soda–lime glass; see Table 1. Interestingly, tin was detected on both sides of the sample. It should be noted that soda–lime glass is made by a float-glass process, which involves melting glass and feeding a thin layer of the molten glass onto a tank of molten tin, protected by an inert nitrogen atmosphere. Therefore, the soda–lime glass surfaces naturally contain some tin, presumably as dissolved SnO that was derived from the manufacturing process. Also, clearly, the upper

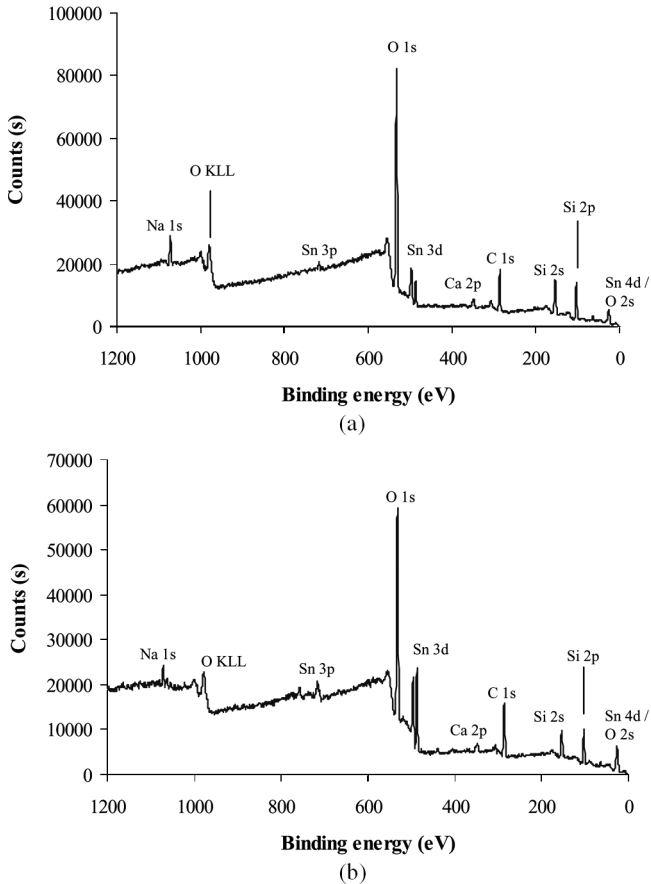
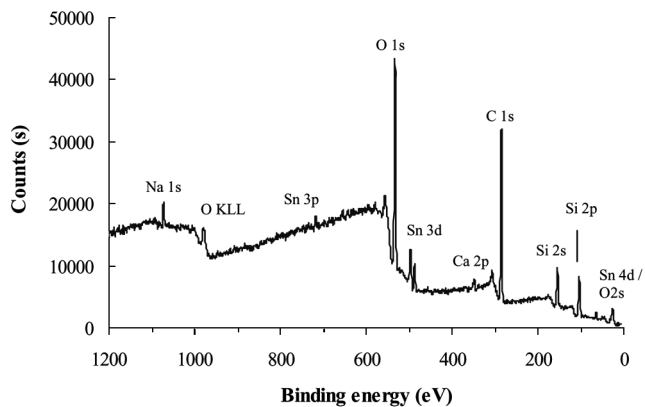


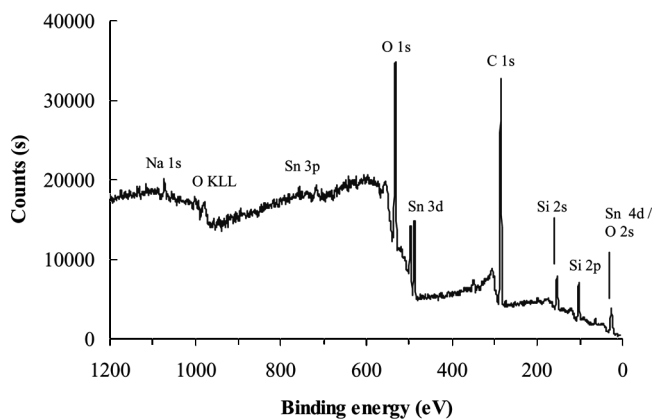
FIGURE 5 XPS survey spectra of the GPS-pretreated samples for (a) side 1 and (b) side 2.

and lower surfaces of the soda–lime glass do not experience the same environment during the forming operation. This results in the bottom surface containing a significantly higher concentration of tin, as compared with the upper surfaces [11]. This obviously explains the different concentrations of tin detected on the two sides of the glass samples. (Note: the side of the glass with a lower concentration of tin will be denoted as side 1 and *vice versa*.)

The XPS survey spectra and the elemental composition of the GPS-pretreated sample are depicted in Figure 5 and Table 2, respectively. The adsorption of the silane onto the glass surface is indicated by the slightly higher concentrations of silicon and oxygen as compared with



(a)



(b)

FIGURE 6 XPS survey spectra of the VTS-pretreated samples for (a) side 1 and (b) side 2.

the simply ultrasonically cleaned glass surface. Also, the intensity of the calcium signal (which originates from the glass) detected on the GPS-pretreated surface was relatively low compared with the intensity detected on the ultrasonically cleaned surface. This implies that an organic overlayer was indeed deposited on the glass surface by the GPS pretreatment. The carbon concentration at 27 to 30% is very close to that recorded in the study of GPS on hydroxylated iron surfaces [12], and it is thus reasonable to assume that the thickness of the GPS layer is comparable at approximately 1.7 nm. This is somewhat thicker than the length of a hydrolysed GPS molecule, which is 1.3 nm. Hence, it appears that the GPS layer exists as a relatively

TABLE 2 Surface Composition (Atomic %) for the Various Glass Substrates

Elements	Ultrasonic cleaning		GPS		VTS	
	Side 1	Side 2	Side 1	Side 2	Side 1	Side 2
C	38.8	38.4	27.0	29.8	54.0	64.0
Ca	1.4	1.6	1.1	1.1	0.9	0.8
N	1.0	0.8	0.3	0.4	—	0.5
Na	1.6	2.4	3.2	1.9	1.7	1.0
O	42.5	42.4	49.4	44.6	30.6	24.1
Si	13.9	11.8	15.8	12.5	11.8	8.3
Sn	0.6	2.6	3.2	9.7	0.6	1.3
Mg	0.2	—	—	—	—	—
Al	—	—	—	—	0.4	—

disorganised layer, with no dominant orientation or structuring [12]. The surface concentration of carbon on the GPS-pretreated glass is significantly lower than that for the ultrasonically treated glass substrate, which on first sight seems counterintuitive, given the previous discussions relating to the deposition of the GPS layer. However, this is not the case; on interaction with the glass the GPS molecules will displace the adventitious hydrocarbon contamination, which is replaced by a more securely bound, but thinner, at about 1.7 nm, layer of the organosilane.

Also, it is noteworthy that a higher intensity of tin was detected on the GPS-pretreated surface than on the ultrasonically cleaned glass surface. This suggests that the tin, which was initially present on the outermost glass surface, has diffused into the polysiloxane layer on the GPS-pretreated glass surface. A similar observation has been reported by Ritter *et al.* [13].

Comparing the XPS survey spectra for the ultrasonically cleaned sample and the VTS-pretreated sample (see Figures 4 and 6), the adsorption of the long alkyl-chain silane on the glass surface is shown by an increase in the intensity of the carbon signal and a decrease in oxygen intensity. The detection of relatively low intensities of the sodium and calcium signals also indicates the presence of the organic silane film on the surface. The shape and intensity of the scattered electron background to a higher binding energy associated with the glass-forming elements Si, Na, O, and Sn, as shown in Figure 6, indicates more energy loss *via* inelastic scattering of electrons, compared with Figure 4. Such a phenomenon is most clearly seen in the spectrum of Figure 6(b) where the regions of the spectrum at a higher binding energy (to the left) of the O1s, OKLL, Si2p, and Si2s peaks

exhibit a much greater intensity than the spectra of Figures 4 and 5. This additional electron intensity is the result of the inelastic scattering of the photoelectrons emanating from the glass in the thicker, uniform organic overlayer (of VTS). This shows that the silane-pretreated surfaces have a thicker layer of organic material present than the ultrasonically cleaned glass surface. Using the Beer–Lambert principle [14], the thickness of the silane layer was estimated to be 3.0 nm. However, the theoretical molecular length of the fully orientated VTS molecule is 3.4 nm and thus this may imply that the silane molecules were adsorbed as a monolayer but at an angle to the glass surface. A simple geometric approach indicates that the molecules are oriented at approximately 60° to the plane of the substrate. On the face of it, this is a surprising observation, as XPS studies of the adsorption of GPS on iron surfaces have shown that the layer thickness may be somewhat greater than the length on the hydrolysed silane molecule [12]. However the reliability of XPS as a means of assessing the orientation of molecules at solid surfaces is well established and has been used to good effect on practical systems. For example, the validation of this approach by using molecular dynamics and XPS analysis of an adhesion failure surface has shown it to be robust and adaptable [15]. Indeed, the fact that the VTS molecules are oriented at approximately 60° to the plane of the substrate has been reported by previous experimental [7] and theoretical studies [8]. Finally, the loss structures associated with the VTS layer discussed previously show that the layer is not present as a patchy overlayer, which would not provide such intense energy-loss structures, giving additional security to the interpretation of the data as a monolayer of VTS molecules in a slanting, rather than normal, orientation.

The spectra of C1s signal were fitted with three peaks corresponding to the hydrocarbon (C–C) at 285.0 eV with the hydroxyl/ether (C–O) at a shift of 1.6 eV relative to the hydrocarbon peak, and the carbonyl/amide (C=O or N–C=O) at a shift of 3.0 eV. The spectrum of the ultrasonically cleaned glass (see Figure 7) is indicative of the usual adventitious hydrocarbon contamination, with the components at 285.0 eV representing the apolar methylene-type contamination, whilst the other higher binding-energy components represent the oxygen-containing polar contamination. Turning now to the C1s spectra of the silane-treated glass surfaces (see Figures 8 and 9), it is obvious that the C–O and C=O peaks detected on the VTS-pretreated surface were relatively less intense than for the GPS-pretreated surface. This observation was indeed expected if the VTS molecules were adsorbed as a monolayer film, and thus confirms the conclusion that the VTS

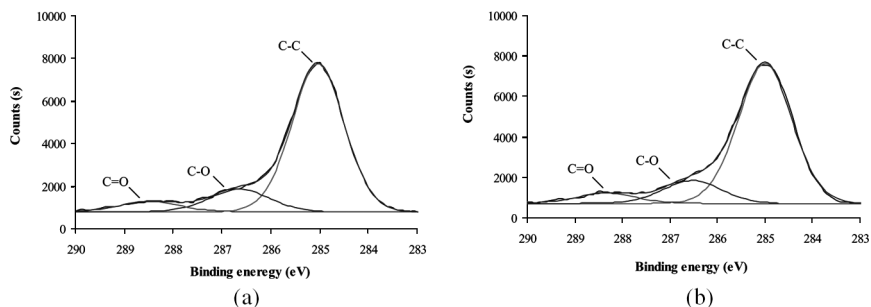


FIGURE 7 High-resolution XPS spectra of the peak-fitted C1s signal for the ultrasonically cleaned glass: (a) side 1 and (b) side 2.

film formed on the glass surface was a monolayer, with the vinyl-terminal groups orientated away from the substrate and the molecules pointing upwards at an angle of about 60° to the glass substrate.

3.3. Fracture-Mechanics Tests

To assess the adhesion properties of the various surface pretreatments, constant displacement-rate tests, based upon a fracture-mechanics approach, were undertaken, as described previously. Figure 10 summarises the values of the adhesive fracture energy, G_C , for the various glass/epoxy/glass DCB joints.

It is apparent that the GPS-pretreated joints exhibited a significantly better performance than the ultrasonically cleaned joints. This observation is in agreement with published work [13,16–18], where the use of such silane-coupling agents has been widely reported to enhance the interfacial adhesion between the glass substrate

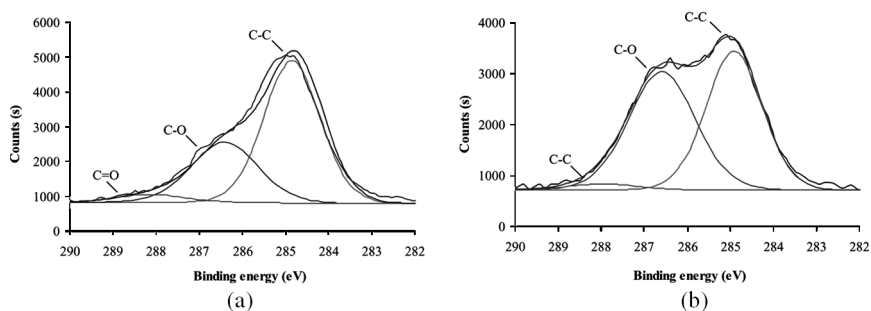


FIGURE 8 High-resolution XPS spectra of the peak-fitted C1s signal for the GPS-pretreated glass: (a) side 1 and (b) side 2.

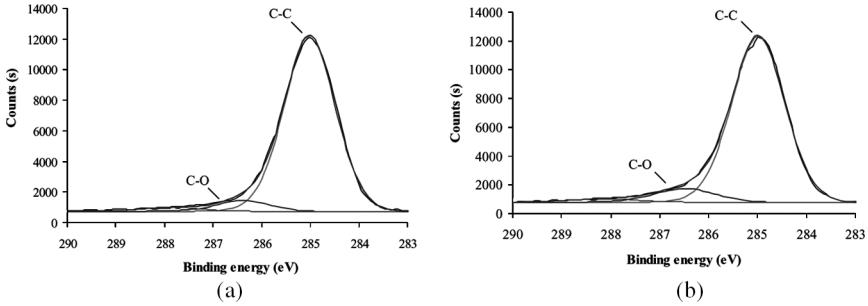


FIGURE 9 High-resolution XPS spectra of the peak-fitted C1s signal for the vinyl-terminated long carbon-chain silane (VTS)-pretreated glass: (a) side 1 and (b) side 2.

and the adhesive. The superior durability performance of the GPS-pretreated joints is attributed to the formation of covalent bonds between the silane coupling agent and the glass surface and between the silane coupling agent and the adhesive [1,2,5]. Thus, the ingressing moisture at the crack tip must now rupture covalent $-\text{Si}-\text{O}-\text{Si}$ bonds, rather than solely the secondary bonds that act across the adhesive/substrate interface of the ultrasonically cleaned joints. This results in crack propagation in the GPS-pretreated joints occurring at relatively high values of G_C .

It may be seen from Figure 10 that the values of G_C ascertained for the joints where the substrates were pretreated with the VTS were relatively very low, compared with the values for the ultrasonically

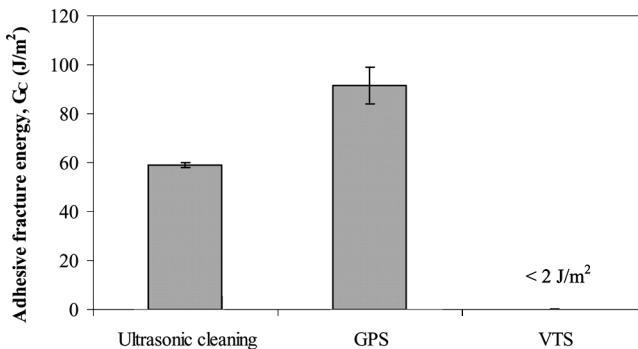


FIGURE 10 Values of the adhesive fracture energy, G_C , for various types of the glass/epoxy/glass DCB joints tested in an aqueous environment. The crack velocity for these tests was 0.3 mm/min. The error bars represent the standard deviations.

cleaned joints and the GPS-pretreated joints. This is as expected and arises from the relatively poor wetting and intrinsic adhesion between the epoxy and the vinyl-terminal groups of the VTS silane, because such vinyl groups are unreactive with respect to the epoxy and are also apolar, as discussed previously.

4. CONCLUSIONS

The use of a novel vinyl-terminated long alkyl-chain self-assembling silane (VTS) with a 20 alkyl-chain length has been assessed as a primer for epoxy/glass joints. A relatively high contact angle of 83° was found for water on the VTS-pretreated soda–lime glass surface. This revealed that the degree of hydrophobicity of this surface was far more pronounced than for the ultrasonically cleaned glass surface or the γ -GPS-pretreated glass surface, which gave contact angles of 14° and 42° , respectively. Further, good agreement between the measured and the theoretical contact angles for a fully adsorbed vinyl-terminated SAM surface implied that the VTS molecules were adsorbed with the vinyl-terminal groups orientated away from the glass surface. Indeed, XPS analysis confirmed that the VTS molecules were adsorbed as a monolayer with the vinyl-terminal groups orientated away from the glass surface. XPS also revealed that the adsorbed VTS molecules that formed the monolayer were inclined at an angle of about 60° to the glass surface. These conclusions were borne out by the results from the fracture-mechanics tests, where the adhesive fracture energy, G_C , for the VTS-pretreated glass/epoxy/glass joints was relatively very low compared with the ultrasonically cleaned joints and the GPS-pretreated joints.

The very low values of G_C for the VTS-pretreated joints may lead to this novel long alkyl-chain silane finding applications as an adhesive coating. However, on the other hand, an advantage of the vinyl-terminal groups is that it may be possible to activate these functional groups so that they are then able to chemically react with an epoxy adhesive to form covalent bonds between the adhesive and substrate. Also, in a long alkyl-chained silane, the intermediate alkylchains would be highly hydrophobic, so such an ordered monolayer film would impede water diffusing through the monolayer to the silane/substrate interface. All of these features should help to impart excellent joint durability. This work is currently in progress.

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