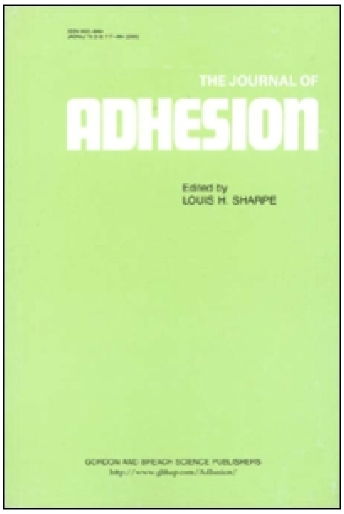

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Adhesion Promotion by Silanes: A Study of their Interfacial Chemistry in a Model Polystyrene Coating by XPS and SIMS†

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Adhesion of a polystyrene coating to solvent cleaned steel is increased two-fold by addition of 0.5% wt/wt of aminosilane (A1120). A study has been carried out on the coating-substrate interfacial chemistry to gain an understanding of the mechanism of adhesion promotion. It is shown that in peel experiments the coating fails adhesively between the polystyrene and an adsorbed layer of aminosilane on the steel surface. The improvement in adhesion results from displacement by the silane of the 1.4 nm thick layer of residual carbonaceous contamination on the steel surface. It is proposed that this leads to a stronger substrate-coating interaction either through improved intermolecular contact between the segregated silane and the polymer or through secondary bonding between the amine groups of the silane and the polarisable aromatic rings of the polystyrene.

KEY WORDS Adhesion promotion; coatings; coupling agents; secondary ion mass spectrometry (SIMS); silanes; X-ray photoelectron spectroscopy (XPS).

INTRODUCTION

Organofunctional alkoxysilanes are frequently used as adhesion promoters for organic resins, particularly when improved durability in wet environments is required. In the simplest model it is

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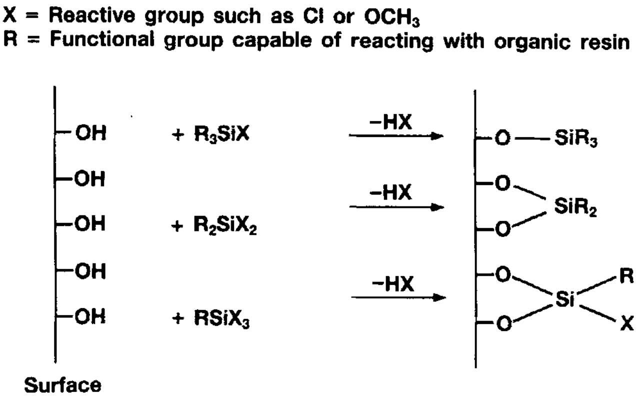


FIGURE 1 Interaction between organofunctional silanes and substrates with surface hydroxyl groups (accepted mechanism).

considered that silanes act as a coupling agent linking substrate surface hydroxyl groups to the resin, in the manner shown in Figure 1, though the silane may be more than one molecular layer thick. This results in a bond which is more stable to the ingress of water than the van der Waals' forces which are the usual basis of adhesion.

Silanes have been used for many years in glass fibre reinforced plastic (GRP) manufacture, applied from aqueous solution as a primer to enhance bonding between glass fibre and resin matrix. They have also been used in the same way as primers for the adhesive bonding of metals. The interfacial chemistry of these layers has been reviewed.[1-3] There is evidence for the formation of direct Si—O—substrate chemical bonding, but when applied as a primer coating from aqueous solution a thick layer (>10 nm) of siloxane polymer forms. This occurs through crosslinking of Si—OH groups in the hydrolysed silane. The mechanism by which these thick layers promote adhesion remains, however, poorly understood.

Silane adhesion promoters are also often incorporated in adhesive or coating resin formulations to improve initial strength and durability. In an organic medium hydrolysis of the silane cannot occur (except with aqueous impurity). Reaction is then limited to the surface hydroxyl groups, with film formation limited to a monolayer. Little work has been reported on the mechanism of adhesion promotion by silanes under these conditions. Preliminary work carried out in our laboratories indicated that silanes could give beneficial improvements in adhesion even when incorporated in solvent dried coatings where the reaction with the resin coatings could not occur.

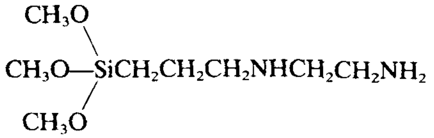
The aim of this study was to gain a better understanding of the mechanism of operation of silane adhesion promoters when added to a resin applied to a steel surface. Polystyrene was chosen as a model non-reactive resin. Since it contains only hydrogen and carbon atoms the use of polystyrene both simplifies and enhances data interpretation. The silane used was A1120, a diaminofunctional methoxysilane. In this model system no primary chemical bonding can occur between the adhesion promoter and the resin.

The chemistry of the resin-steel interface and the interactions of the silane promoter with the steel have been studied using X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). These techniques are sensitive to the outermost few atomic layers providing elemental and functional group analysis of an exposed surface. Combined with adhesion test measurements, the surface analytical techniques enable information about the molecular basis of adhesion to be obtained.

EXPERIMENTAL

Materials

The adhesion promoter used was a commercially available aminosilane, A1120, which was obtained from Union Carbide and has the following structure:



$$\begin{array}{l} \quad\mathrm{CH_3O} \\ \qquad\quad\backslash \\ \mathrm{CH_3O{-}SiCH_2CH_2CH_2NHCH_2CH_2NH_2} \\ \qquad\quad / \\ \quad\mathrm{CH_3O} \end{array}$$

The steel was 22 swg polished mild steel sheet (BS1449 grade CR1 1972) cut from standard paint test panels obtained from the Pyrene

Company Ltd. The polystyrene (BDH Ltd) had a molecular weight of approximately 100,000.

Sample Preparation

Coating samples were examined in a VG ESCALAB instrument using a T-peeler device manufactured by VG Scientific Instruments. The T-peeler attachment is mounted in the preparation chamber of the spectrometer and allows separation of coating from metal within the vacuum system of the spectrometer. This enables the interfaces to be examined without the complication of contamination or degradation by the environment after separation. Samples were transferred within the vacuum system to the appropriate chamber for analysis by either XPS or SIMS.

The steel as supplied is covered in a rust-inhibiting oil. This was removed with trichloroethylene in an ultrasonic cleaning bath. The coating used was a solution of polystyrene resin (25% wt/wt dissolved in toluene) which had a Brookfield viscosity of 380 centipoise. It was allowed to dry by solvent evaporation in air for 72 h at 23°C and 50% relative humidity. Peeling detached the polystyrene from the metal revealing the underside of the coating (polymer interfacial surface) and the metal (metal interfacial surface). A sample of the cleaned steel was also prepared as a reference.

To study the effect of the adhesion promoter a second series of T-samples was prepared. This had 0.5% wt/wt of the aminosilane added to the polystyrene coating solution. Since the coating dries by solvent evaporation this is equivalent to 2% of the solid coating weight. Finally, a film of polystyrene was cast onto a mild steel test piece and analysed to obtain the oxygen content of the surface of bulk polystyrene.

Adhesion Tests

In addition to peeling, the adhesion strength of the coating was determined independently using a torque/shear adhesion test.[4]

Adsorption Studies

Steel samples (1 cm^2) were treated with dilute solutions of the coupling agent and analogues of its silane and amine components, *viz* tetramethoxysilane and N-isopropyl ethylenediamine, to investigate separately the effect of the diamine and methoxy functional groups. The same type of steel was used as for the T-peel experiments but cleaning was by filing under toluene (Aristar grade). This produces a surface with a lower and reproducible level of carbon contamination which aids interpretation of the results. The samples were treated for 60 s with 10 cm^3 of a 1% wt/wt toluene solution of the appropriate additive and then rinsed three times (60 s each) in fresh toluene. The washing ensures that only additives which chemisorb on the steel remain on the steel surface. Each sample was analysed first by XPS then by SIMS. A reference sample was prepared in the same way without any additive.

Surface Analysis

XPS spectra were obtained with the ESCALAB instrument using the constant analyser energy (CAE) mode, a pass energy of 50 eV and AlKα X-rays at 250 W. Pressure in the analysis chamber was below 10^{-8} mbar during the experiments. Peak areas were determined and appropriate sensitivity factors[5] used to calculate elemental compositions for the surfaces.

These are presented as atom concentrations (excluding hydrogen) in Tables I–IV. For a surface which is homogeneous within the XPS sampling depth (up to ~9 nm) this is the composition of the exposed surface. If, however, the surface is inhomogeneous, the accuracy of the composition determined by XPS is uncertain. For example, when there is a thin continuous overlayer on an iron surface the contribution to the total signal from the iron, i.e. the apparent iron concentration, depends on the thickness of the overlayer.

In addition to elemental composition, XPS provides information on the chemical states of the elements. The carbon peaks had complex peak envelopes due to the presence of multiple carbon-oxygen functional groups. These were analysed using a computer curve fitting program, assuming the envelope to consist of the following components: carbon singly bonded to oxygen (C—O), e.g. hydroxyl or ether, carbonyl (C═O) and carboxyl at binding energies, +1.6, +3.0 and +4.2 eV relative to the hydrocarbon peak. In the routine, peak width and energy were fixed and only peak heights were varied for each component to obtain optimum fit between experimental and synthesised spectra.[6] Contributions from C—N groups at +1.0 eV cannot be fitted separately in the presence of C—O groups at +1.6 eV. The reported concentration of C—O may therefore contain a contribution from the nitrogen groups.

Positive and negative SIMS spectra were obtained using an argon ion beam current of 50 nA rastered over an area of 10 mm^2.

RESULTS AND DISCUSSION

Surface Composition of Steel Substrate

The surface composition of the solvent-cleaned steel substrates used in this study is shown in Table I. Apart from low level contamination from chlorine, sodium and nitrogen, the major contribution to the XPS spectra arises from iron, oxygen and carbon, the latter arising from a tenaciously held overlayer of carbonaceous contamination approximately 1.4 nm thick. The iron spectra show peaks due to both iron metal and oxide with a relative intensity suggesting that the oxide film is, on average, 3.2 nm thick. The nature of the carbonaceous contamination is indicated by the C(1s) spectrum shown in Figure 2. This shows a broad distribution of carbon states, the major species being hydrocarbon, with significant proportions of the possible carbon-oxygen species, ether/hydroxyl, carbonyl and carboxyl, also being present.

TABLE I
Composition of solvent cleaned steel surface

(Atom percent)	
Carbon	38.7
Oxygen	43.8
Iron	16.7
Nitrogen	0.2
Silicon	0
Chlorine	0.4
Sodium	0.2

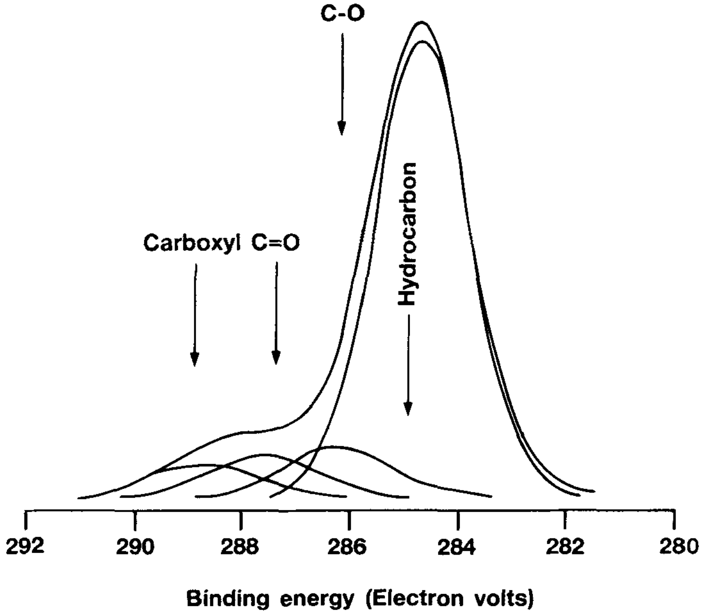


FIGURE 2 Carbon (1s) peak with peak synthesis of the XPS spectrum of mild steel as cleaned prior to coating.

Adhesion Promotion of PVC/PVA Coatings by Silanes

The results of an investigation of the use of silanes with non-curing resins, referred to in the introduction, is summarised in Table II. The coating was a PVC/PVA copolymer (Union Carbide VAGH) applied as a 25% wt solution in organic solvent. Silanes were added at 0.5% wt and the coating applied to mild steel and allowed to dry

TABLE II
Pull-off adhesion of vinyl resin (VAGH) with added coupling agents

Additive	Formula	Adhesion N/mm^2
Control	—	7.8
Silane A1100	$(C_2H_5O)_3Si(CH_2)_3NH_2$	20
Silane A1120	$(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$	21.8
Silane A171	$(CH_3O)_3Si(CH_2)_3CH{=}CH_2$	8.0

by solvent evaporation. The effect of the silanes on bond strength was determined by the pull-off method.[7] Very large increases in adhesion, nearly threefold, were obtained with the two aminofunctional silanes. The PVC/PVA resin does not have functional groups capable of forming primary chemical bonds with the amine functional group of the silane. The importance of the amine groups, however, is shown by the fact that the vinyl functional silane gave no significant increase in bond strength over the untreated sample. For all three silanes, examination of the failure surfaces by XPS showed evidence of silane segregation from the bulk resin to the polymer/metal interface. Since the diaminofunctional silane gave the best overall result it was chosen for investigation in the present study.

Polystyrene Coatings

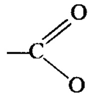
The results of the torque/shear adhesion tests on the polystyrene coatings are given in Table III. They show that addition of 0.5% wt of the A1120 diamino-silane doubles the adhesion strength of the coating. The T-peeler result which showed an 80% increase in strength when using the silane confirms the adhesion promotion effect.

TABLE III
Composition of separated surfaces (atom percent)

Element	Sample 1 No Silane PIS	MIS	Sample 2 1% aminosilane PIS	MI
Carbon	98.2	37.4	96.9	49.6
Oxygen	1.4	43.9	1.7	31.7
Iron	0	17.2	0	11.8
Nitrogen	0	0.6	0.8	3.6
Silicon	0.2	0	0.6	2.3
Chlorine	0.1	0.5	0.1	1.0
Sodium	0	0.4	0	0.1
Torque-shear adhesion strength N/mm^2	6.8 ± 0.9		13.3 ± 1.9	

PIS = Polymer Interfacial Surface.
MIS = Metal Interfacial Surface.

TABLE IV
Carbon (1s) functional group analysis of separated surfaces (atom percent)

	Hydrocarbon	C—O	—C=O	 $-\mathrm{C}{\overset{\mathrm{O}}{\diagup} \atop \underset{\mathrm{O}}{\diagdown}}$	Shake up
	285 eV	286.6 eV	288 eV	289.2 eV	292 eV.
PIS (both samples)	94.0	0	0	0	4.3
MIS/no silane	30.8	2.5	2.8	1.4	0
MIS/aminosilane	40.5	8.4	0	0.3	0
Metal as cleaned	30.0	3.3	2.7	2.2	0

PIS = Polymer Interfacial Surface.
MIS = Metal Interfacial Surface.

The elemental surface analyses are summarised in Table III. Carbon (1s) peak synthesis data are given in Table IV. The results show that in all cases the two separated surfaces of each T-peel specimen have very different compositions; this is indicative of truly adhesive failure occurring along a phase boundary. Adhesive failure at the molecular level is confirmed by the difference in shape of the C(1s) spectra of the two surfaces. This can be clearly seen in Figures 3 and 4 which are the spectra for the sample without coupling agent. In addition, on all samples, iron and oxygen are found at high concentrations on the metal interfacial surface. No iron was detected on the polymer interfacial surfaces although there was a trace amount of oxygen. The binding energy of this oxygen (533.5 eV) shows it to be of organic origin and therefore not due to iron oxide from the metal.

For the untreated samples (no silane) the C(1s) spectrum of the polymer interfacial surface (Fig. 3) shows a large hydrocarbon peak together with a shake-up peak at 292 eV binding energy. This peak is characteristic of the presence of the aromatic ring in polystyrene. The metal interfacial surface (Fig. 4) has a lower hydrocarbon concentration together with a distribution of carbon/oxygen species (binding energies 286.6–289.2 eV). These are typical of the thin layer of residual contamination always found on solvent-cleaned steel (Fig. 2). Oxygen concentrations on the metal interface were high and characteristic of iron oxide.

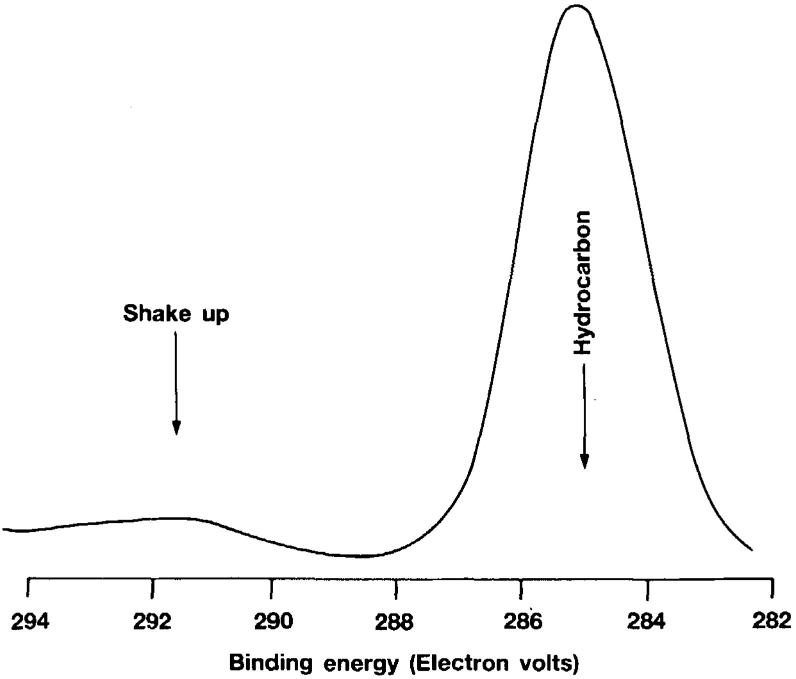


FIGURE 3 Carbon (1s) region of the XPS spectrum of the polymer interfacial surface of a T-peeled polystyrene coating (no silane).

The iron was present predominantly as oxide but with a lower binding energy shoulder on the peak revealing the presence of metallic iron. These results show that when no coupling agent is used true adhesive failure occurs between the polystyrene coating and the layer of contamination on the metal surface.

When the coupling agent is used strong nitrogen and silicon peaks are detected in the XPS spectrum of the metal interfacial surface (Table III). These are due to the presence of aminosilane because only trace amounts of these elements are found on the clean steel or on the failure surfaces of non-promoted specimens. As expected for the aminosilane, the nitrogen is detected at a binding energy of 399.4 eV and the silicon is found at 102.9 eV which is consistent with silicon bonded to oxygen.

The silicon:carbon ratio of 0.046:1 is 38 times greater than the

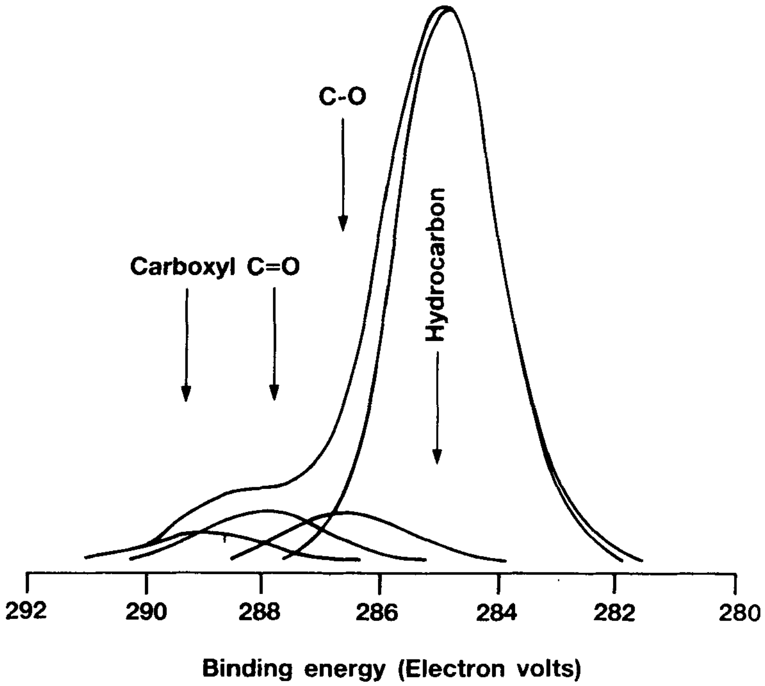


FIGURE 4 Carbon (1s) peak with peak synthesis of the XPS spectrum of the metal interfacial surface of the above (Fig. 3) sample.

ratio of 0.0012:1 present in the coating. It follows that the silane has migrated from the bulk coating to the metal surface during drying of the coating film. If it is assumed that the silane is present as a continuous layer on the metal surface then the observed iron signal of 11.8% indicates a layer thickness of approximately 3 nm. Sufficient silane to produce the observed increase in concentration in such a layer is present in a polystyrene coating only 0.1 microns thick. Since the coating was 50 microns thick the observed increase on the metal surface requires migration of only 0.2% of the total silane present.

The polymer interfacial surface has a very different composition. The silicon:carbon ratio here is 0.006:1 which is only 4 times the bulk value and is little different from that found on the outer surface of the polystyrene film (Table V). Thus, although there is a

TABLE V
Elemental composition of polystyrene surfaces (atom per cent)

Element	Polystyrene film	Polystyrene film + silane	Polystyrene + silane (calculated)*
Carbon	99.9	96.6	99.28
Oxygen	0.1	1.8	0.36
Iron	0	0	0
Nitrogen	0	0.7	0.24
Silicon	0	0.8	0.12
Chlorine	0	0.1	0
Sodium	0	0	0

* Calculated bulk atom per cent composition of dry polystyrene film containing 2 weight per cent aminosilane.

tendency for the silane to segregate to the polystyrene surface during drying, it is clear that adsorption on the metal surface provides a strong driving force. The different compositions of the two interfacial surfaces show that the locus of adhesive failure is between the underside of the polymer film and the adsorbed silane layer on the metal surface.

The nitrogen:silicon ratio of 1.5:1 detected for the silane layer is lower than the atom ratio of 2:1 present in the silane molecule. If the additive binds as usually supposed, i.e. *via* silicon-oxygen bonds to the metal surface, then some additional shielding might occur, reducing the silicon concentration relative to nitrogen. The fact that the opposite occurs suggests that instead the amine groups might be oriented towards the metal surface. The C(1s) spectrum for this surface (Fig. 5) has a different shape from that of the clean metal or the metal of the polystyrene only sample. Peak synthesis (Table IV) shows an approximately three-fold increase in the peak due to C—O/C—N species. This is attributed to the methoxy and amine groups present in the coupling agent and is sufficiently large to suggest that not all the hydroxy groups are hydrolysed during formation of the layer. Another important feature is that the C=O and carboxyl functional groups originally present on the metal are absent. There is not sufficient material present on the metal surface to account for this by assuming the coverage of the contamination

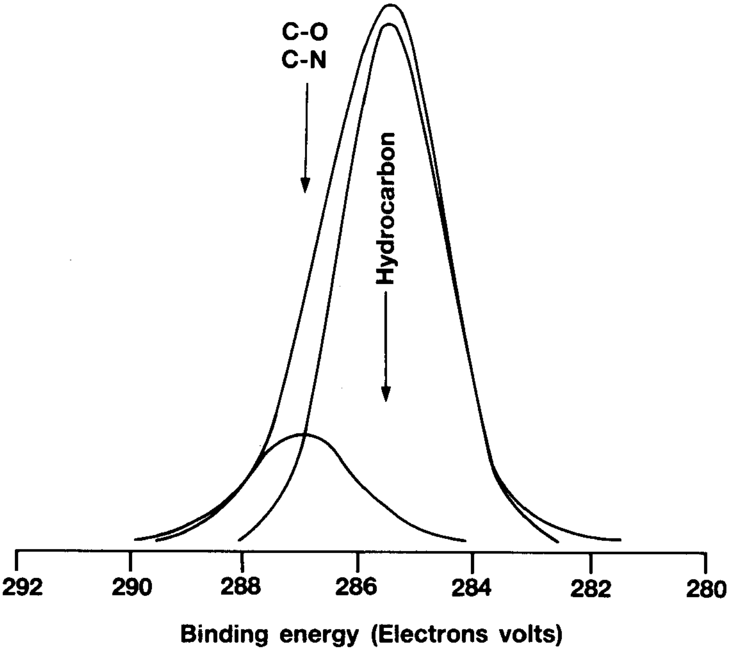


FIGURE 5 Carbon (1s) peak with peak synthesis of the XPS spectrum of the metal interfacial surface of a T-peeled polystyrene coating (silane treated sample).

by another layer. It follows that during adsorption of the silane a large proportion of the carbonyl and carboxyl contamination has been displaced.

The hydrocarbon concentration of 40.5 atom per cent is too large to be attributed solely to the carbon present in the silane. It may partially be due to residual contamination not displaced by the silane but there is also evidence from a weak shake-up peak that some polystyrene is incorporated into the metal interfacial surface layer.

Considering the XPS and adhesion results together it can be seen that the aminosilane increases adhesion by segregating to the metal surface where it displaces surface contamination to form a strongly bound surface layer. It is not possible for the silane to chemically react with the polystyrene, therefore failure now occurs between the

TABLE VI
XPS data for compounds adsorbed on clean steel surface (elemental composition (atom per cent)

Element	Control no additive	Tetramethoxy silane	N-isopropyl ethylene-diamine	Amino-silane A1120
Carbon	26.1	22.7	22.7	23.6
Oxygen	44.3	48.8	46.1	43.5
Iron	29.2	27.3	28.8	23.0
Nitrogen	0.13	0.43	1.7	4.1
Silicon	0	0.25	0	2.2
Chlorine	0.4	0.5	0.7	0.8
Sodium	0	0.3	0	0

adsorbed silane layer and the polystyrene coating. The improvement in strength is attributed to improved physical interactions at this new interface.

Adsorption Studies

Further information on the interaction between the aminosilane and steel surfaces was obtained from the results of the adsorption studies. Table VI summarises the XPS results. These provide very strong evidence for the displacement of surface contamination by the aminosilane. The carbon level on the treated sample (23.6%), compared with the untreated surface (26.1%), is not increased by the silane adsorption. Furthermore, as there are 8 carbon atoms to every silicon in the aminosilane, most of this carbon (17.6%) is attributable to carbon in the adsorbed silane. Thus approximately 80% of the contamination is displaced by the aminosilane. The silicon level of 2.2 atom per cent is similar to be found in the T-peel experiment but the N:Si level of 1.85:1 is closer to the expected 2:1.

The aminosilane contains both diamine and methoxy functional groups. Two compounds, tetramethoxysilane and N-isopropyl ethylenediamine, were used in adsorption experiments to model independently the interactions between these groups and the metal surface. The XPS results for steel treated with solutions of these compounds in toluene are given in Table VI. For the diamine sample 1.7 atom per cent of nitrogen is detected corresponding approximately to monolayer adsorption of the molecule. The silicon from the tetramethoxysilane is only just detectable indicating that coverage is less than a monolayer. These results show that both the methoxysilane and diamine functional groups are capable of chemisorbing onto the steel surface. If the molecules were only physisorbed they would be removed during the triple washing of the samples with toluene or in the vacuum system of the XPS instrument.

When the aminosilane was adsorbed in this way the surface coverage (N 4.1%, Si 2.2%) was greater than by either of the two model compounds. This is consistent with the observation of Chiang[8] that amines in aminosilanes can catalyse the formation of Si—O—metal bonds.

The results from the SIMS experiments on the aminosilane-treated steel sample (Figs. 6 and 7) show peaks due to species

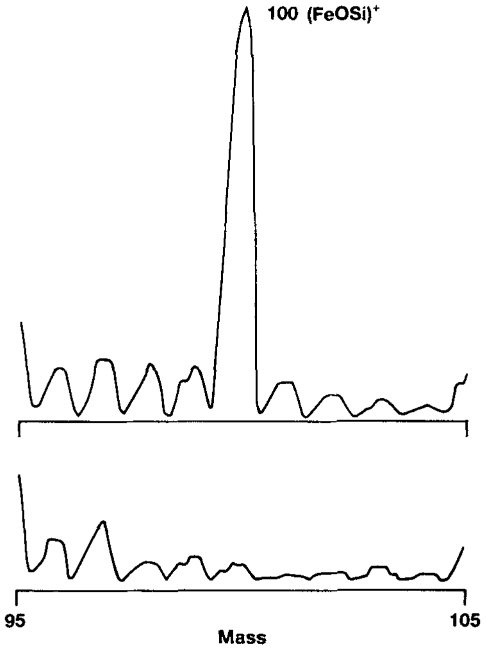


FIGURE 6 Positive SIMS spectrum of aminosilane treated mild steel (top) compared with that of untreated steel.

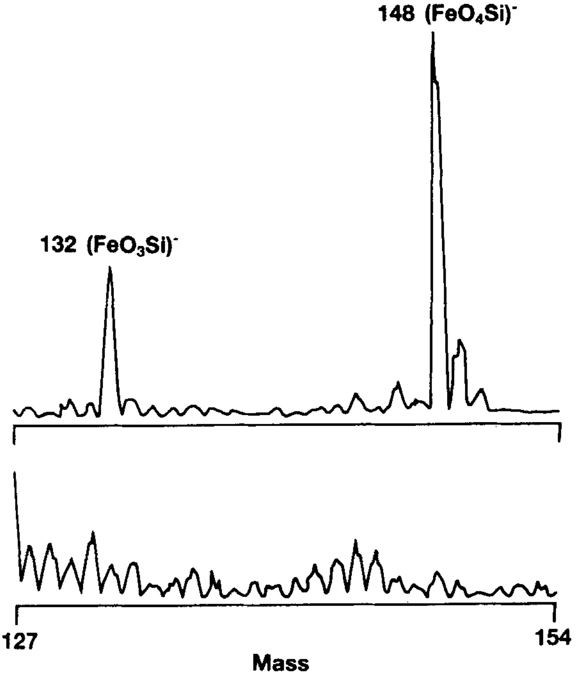


FIGURE 7 Negative SIMS spectrum of aminosilane treated mild steel (top) compared with that of untreated steel.

containing iron, oxygen and silicon bound together which do not appear in the spectra of the untreated sample. A peak at mass 100 assigned to $(FeOSi)^+$ has previously been reported by Gettings and Kinloch[9] in a study of an epoxy functional silane applied from aqueous solution onto steel. Silanes applied from aqueous solution are known to form polysiloxane layers > 10 nm thick.[2] In the present work on silane monolayers applied from organic solvent the simultaneous appearance of three peaks at masses 100 $(FeOSi)^+$, 132 $(FeO_3Si)^-$ and 148 $(FeO_4Si)^-$ is strong evidence for chemical bond formation between the aminosilane and the iron *via* Si—O—Fe bonds. This is a particularly important result as it shows that chemical bonding of the silane to substrate can occur in the absence of bulk water as is the case when silanes are added to adhesives or coatings. Similar but smaller peaks were observed in the SIMS spectra of the tetramethoxysilane sample; this is in keeping with the lower concentration observed by XPS. Unfortunately, the SIMS experiments are unable to distinguish any species due to interactions between iron and amine groups because of coincidences of masses in the spectra.

MECHANISM OF ADHESION PROMOTION BY SILANES

It is clear that an important part of the mechanism by which the aminosilane increases adhesion, is its ability to segregate from the resin to the metal surface where it displaces surface contamination to form a strongly bound surface layer (bonded either *via* the silicon or the nitrogen groups). As it is not possible for the silane to react chemically with the polystyrene, failure now occurs between the adsorbed silane layer and the polystyrene coating.

Since the silane exhibits surface active behaviour, it might be expected that the increased adhesion is due to improved resin/substrate contact as a result of better wetting of the steel when the silane is present in the resin. However, both formulations showed spontaneous spreading over the steel surface. The increase in strength must therefore be attributed to improved physical interactions across the new interface, i.e. stronger intermolecular interactions between the polystyrene and the chemisorbed silane (compared with the interactions between polystyrene and the residual carbonaceous layer present in the absence of silane). The improvement may occur as a consequence of the silane molecule, having segregated from the resin, experiencing a more effective molecular overlap with the polymer chains. Alternatively, one would expect a stronger secondary interaction between the adsorbed silane and the polymer arising from polar interactions between the dipole on the amine group and the polarisable aromatic rings in the polystyrene.

This study has shown that even where no primary chemical bonding can occur, significant improvements in adhesion strength are obtainable through the use of monolayer quantities of appropriate adhesion promoter at the resin-substrate interface.

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