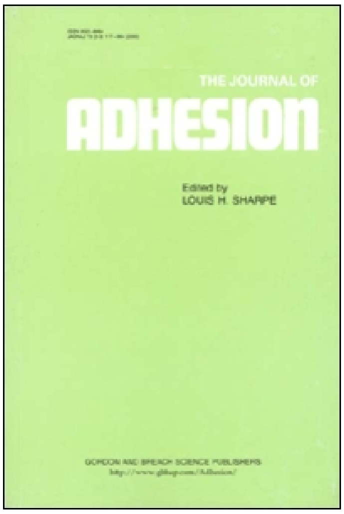

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K. W. Allen[a]; M. G. Stevens[ab]
[a] Adhesion Science Group, Department of Chemistry, The City University, London, England [b] Department of Materials Science, New South Wales Institute of Technology, Sydney, Australia

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The Structure of Films of Silane Primers on Aluminium Substrates

K. W. ALLEN and M. G. STEVENS†

Adhesion Science Group, Department of Chemistry, The City University, London, EC1V 0HB, England

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Specular reflectance infra-red spectroscopy has been used to elucidate the structure of thin films of silane coupling agents on aluminium. Changes in the hydroxyl absorption band at 3400 cm^{-1} were linked to thickness changes and to increasing hydrogen bonding and chelation. This suggests chemical bonds linking silane and metal. Only with the thinnest films is hydroxyl bonding dominant and able to influence the coherence of the silane film.

INTRODUCTION

The use of primers composed of organo siloxanes in adhesive joints with metal substrates is well established as a means of improving durability especially in moist conditions. Generally, this improved durability can be achieved without any loss of initial strength. Sacco and Tanner[1] demonstrated that with adherends of aluminium alloys 2024T3 and 6061T4 and an epoxy adhesive, glycidoxypropyltrimethoxysilane as primer increased the bond strength by 29% and mercaptopropyltrimethoxysilane primer increased the bond strength by 43% although 2-aminoethyl,3-aminopropyltrimethoxysilane and a vinylbenzylamine functional silane primer generally gave no significant increases or even slight decreases in strength. These gains refer to testing under dry conditions and are quite apart from the effects upon durability.

De Lollis[2] working with glycidoxypropyltrimethoxy silane on aluminium adherends and urethane adhesives found no significant change in joint strength consequent on the use of the primer under dry conditions.

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† Present address: Department of Materials Science, New South Wales Institute of Technology, Sydney, Australia.

Bascom[3] reports several instances where the dry strength of bonds with silane primers increased very considerably, as well as some where the change was negligible.

It has been supposed that the films of the silanes involved as primers in these situations were not only bonded to the two different materials but were also cross linked themselves to form a silane polymer. This is supported by the work of Stromberg, Tutes and Passaglia[4] who used ellipsometry to show that silane films on glass or steel grew to a constant thickness corresponding to between 4 and 10 molecules thick depending upon the precise materials used. Bascom[5,6] confirmed these conclusions in a series of studies using ellipsometry, attenuated total reflectance infra-red spectroscopy and contact angle measurements.

All this would lead one to anticipate that films of polymerised silane should be of considerable mechanical strength otherwise they would constitute a weak layer within adhesive joints. However, in a study of rather thick films of silane prepared by hydrolysis and casting in isolation from any bonding surface, Allen, Hansrani and Wake[7] found them to possess very slight mechanical strength. They concluded that the films were not continuous but particulate in structure and that the extent of polymer cross linking was very restricted. The structure possibly involved six membered rings and short connecting chains with free hydroxyl groups protected by a spiral structure. Such a structure is supported by the work of Fox, Taylor and Zisman[8] on the behaviour of a series of linear polymethyl siloxanes spread on water. It was revealed that these compounds could coil reversibly into helices with about six monomers per turn and in liquid of moderate thickness this represented the configuration. When spread as thin films (monomolecular or near to this) on water the helices uncoiled and the molecules were arranged with the long axis on the water surface.

The present study was to explore the structure of films of γ-glycidoxypropyltrimethoxysilane spread on aluminium and to contrast this with the results for the thicker films which had been prepared in isolation.

EXPERIMENTAL

Materials

For various parts of the work different grades of aluminium were used as adherend:

i) Aluminium alloy 6082 (HE 30) containing significant amounts of copper, magnesium silicon and manganese, used in an age-hardened, quenched and extruded form.

ii) Commercially pure aluminium 1200 (EIC), a 99% pure metal which had been cold worked to give a highly stressed, work hardened surface.

iii) Clad aluminium alloy 2014A (BS 2L73) with a surface 99.7% minimum aluminium.

iv) Domestic oven foil, 18 μm thick and 99.9% aluminium with a vegetable oil lubricant on the surface.

A preliminary examination was made of the first two by optical microscopy on unetched specimens. It showed that the first alloy had a matrix probably the face centred cubic aluminium α phase, with a very considerable proportion (40–50%) of a second precipitated phase perhaps the $CuAl_2$ θ phase, while the second had a similar matrix with only a little ($\sim$ 1%) of the precipitated phase. When this nominally pure metal was annealed at 300°C for 45 minutes to relieve the stresses in the worked surface the proportion of precipitated phase increased markedly ($\sim$10%). Examination of electropolished and etched specimens showed no additional phases but revealed the grain boundaries of the matrix oriented preferentially in the direction of rolling. While it was possible to achieve a good finish to the aluminium by conventional metallographic techniques, it was difficult and very time consuming to produce a mirror finish. Electropolishing yielded good results much more rapidly. However the best and most reliable results for reflectance spectroscopy were achieved by evaporation from high purity aluminium wire (99.999% Al) on to clean glass surfaces at approximately 10^{-6} torr. Films of about 0.3 μm were prepared and are reported[9] to develop an oxide film 25–100 Å thick very rapidly on exposure to air.

The silane primer used in all this work was γ-glycidoxypropyltrimethoxysilane available commercially as Union Carbide A187. This type of primer is commonly used in dilute (0.5 $\sim$ 5.0%) acidic solutions in either water or dilute alcohol/water solutions. After application to the metal surface by dipping or brushing, the solution is allowed to dry by exposure in the air. It was decided to use the silane as a 1% solution in twice distilled water of pH 5.0 and allowed to stand for $\frac{1}{2}$ to 1 hour before use. This was thought to be sufficiently acidic to achieve hydrolysis of the silane and would obviate the additional complexity of added acid.

The adhesive used in preparing test joints was Araldite AV100/HV100 a two part epoxy-polyamide adhesive made by Ciba-Geigy Ltd.

Adhesive tests

To demonstrate the efficiency of the silane primer a series of single lap joints were prepared with and without the primer. The adherends were 1 inch wide and with $\frac{1}{2}$ inch overlap prepared by immersion in potassium dichromate/sulphuric acid solution for 10 minutes at 60°C. The joints were assembled with a glue-line thickness of 0.3 mm and were allowed to cure at room temperature for 24 hours before testing. Five specimens were prepared without primer and gave a sheer strength 6.6 ± 0.8 MPa with a predominantly adhesive mode of failure; while five specimens prepared with silane primer gave a shear strength of 11.4 ± 0.8 MPa with a predominantly cohesive mode of failure.

Chemical nature of the uncured silane

At a later stage in consideration of the results questions arose about the purity of the silane primer and particularly about the possible presence of unsaturation in the molecules. To explore this the reaction of the commercial silane used was examined with bromine dissolved in carbon tetrachloride. All the samples reacted with and decolourised the bromine. It had been suggested[10] that bromination might occur either at the epoxide ring or at the C—Si bond. The test was repeated with 1-chloro 2,3-epoxy propane (epichlorohydrin) where attack could only be at the epoxide ring, and with γ-chloropropyltrimethoxysilane where attack could only be at the C—Si bond. In neither case was any decolouration detected, implying that the reaction with the original silane must result from residual allyl glycidyl ether from the preparation or from adventitious olefin impurities. A proton NMR spectrum and the infra-red transmission spectrum failed to reveal any signal corresponding to the olefinic bond, indicating that the quantity present must be below the limit of detection and quite small. (less than 5%). While it would have been possible to attempt to purify the material by redistillation under reduced pressure, perhaps after bromination to render the unsaturated fraction less volatile, this was not undertaken in the present investigation.

The physical form of silane films on metal surfaces

Optical microscopy at magnifications up to × 1226 of films of silane deposited both on clean aluminium and clean glass surfaces revealed a glassy matrix with various apparently crystalline inclusions in every case. The form of the crystals varied depending apparently upon the rate of evaporation of the silane solution. Slow evaporation producing well formed acicular crystals of up to 1 mm in length but more rapid evaporation producing much smaller irregular crystals. Scanning electron microscopy at magnifications of up to × 3000 confirmed this general morphology.

Infra-red spectroscopy of silane films

Infra-red spectroscopy of films of the silane was carried out using a Perkin Elmer Spectrometer 599. Spectra of liquid samples were obtained using a sodium chloride cell of path length 0.1 mm. Spectra of the silane films on aluminium surfaces were obtained by multiple specular reflectance with the Wilkes MIR-18 Multiple Specular Reflectance Attachment used with the Model 9 Single Beam Internal Reflection Attachment. Aluminium films of mirror finish were prepared by evaporation on glass substrates (as described earlier) and were cleaned by plasma bombardment at 10^{-6} torr. These were immediately immersed in a 1% aqueous solution of the silane A187 for half to three-quarters of an hour. They were then removed, drained to various degrees, and allowed to dry in air at room temperature or slightly above.

A transmission spectrum of the liquid silane A187 showed a considerable number of bands most of which can be satisfactorily assigned in terms of the known structure of γ-glycidoxypropyltrimethoxysilane.

In order to assess the technique of Specular Reflectance a film of silane A187 was cast on an aluminium mirror surface from a 1% solution in anhydrous methanol. This spectrum almost exactly reproduced the previous transmission spectrum of liquid both in position of the bands and in their relative intensities thus validating the technique and its performance satisfactorily.

Thin films produced by the deposition of silane A187 from aqueous solution on aluminium surfaces were investigated and the effects of thickness were explored by the Specular Reflectance Technique. The thickest films were obtained by the evaporation of small volumes of solution, while thinner ones were produced by allowing the solution to drain away from the aluminium mirror surfaces, and the thinnest by following drainage of the solution by washing with distilled water. These spectra were well characterised with a number of bands as is illustrated by a typical spectrum (Figure 1). Rather more detail seems to have been obtained than by Boerio *et al.*[12]

For the thickest films, an estimate of the thickness was made through estimates of the area covered, the weight of silane (from the concentration and volume of the solution) and its density. This gave a value of about 5×10^{-6} m (5 μm) which was probably not to be considered as more than an indication of order of magnitude. Comparison of intensities of some of the infra-red absorptions enabled estimates to be attempted for the thinner films. For the very thinnest films, where a monolayer might be suggested, thickness could be down to 20×10^{-10} m (20 Å).

DISCUSSION

The most obvious and apparent difference between the specular reflectance spectra obtained from silane films cast from aqueous solution and that derived by transmission through the liquid silane is the appearance of considerable broad absorption in the 3400 cm^{-1} region due to the presence of hydroxyl

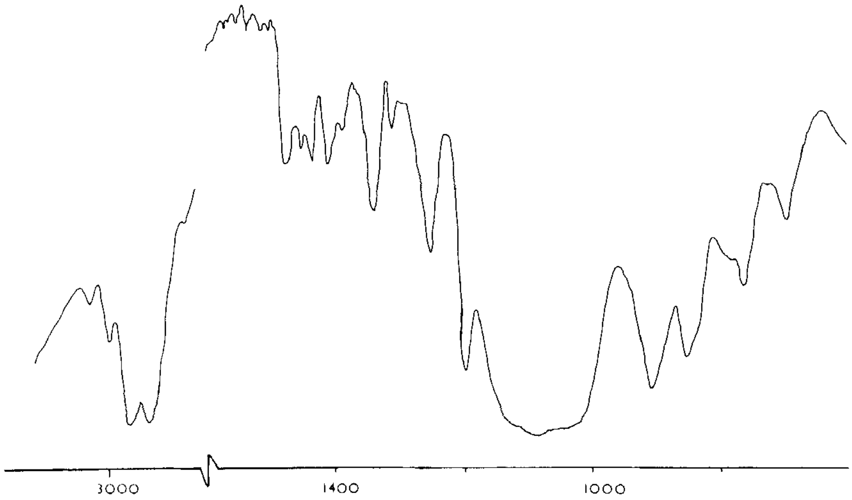

FIGURE 1 Specular reflectance infrared spectrum of silane A187 on aluminium surface.

groups.[11] There is also a group of peaks around 1650 cm^{-1} which is characteristic of the bending vibration of the water molecule. Most of the broad band 770–860 cm^{-1} which has been attributed to alkoxy groups is no longer present in the spectra of the hydrolysed films. A very broad band appears stretching from 1000 cm^{-1} to 1150 cm^{-1} in place of rather less intense individual peaks, which may indicate cross-linking through Si—O—Si bonds.

TABLE I

Variation of infra-red absorption frequency with thickness of silane film

Film characteristics Approximate thickness (calculated)	Method of preparation	Absorption bands
1 ~ 10 μm	Thick film. Few ml solution allowed to evaporate	Bands very intense 3400 cm^{-1}
0.01 ~ 0.10 μm	Medium film. Aluminium allowed to drain before drying.	Bands of moderate intensity 3380 cm^{-1}
0.001 ~ 0.10 μm	Thin film. Aluminium allowed to drain before drying.	Bands of low intensity, ordinate expansion helpful 3350 cm^{-1}
~0.001 μm	Only a very few molecules thick. Well washed with water after drainage.	Bands of very low intensity, only significant when magnified × 10. 3200 cm^{-1}

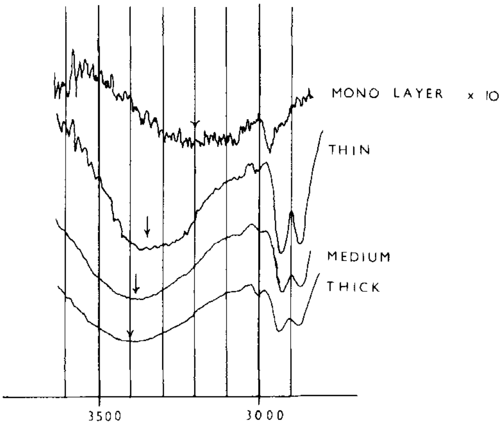

FIGURE 2 Variation in Specular Reflectance Infrared spectrum of silane A187 on aluminium as a function of thickness of silane.

The bands at 2840 cm^{-1} and 1180–1200 cm^{-1} which are characteristic of the Si—O—CH_3 grouping are also closely similar in position to bands characteristic of the C—Si bond in compounds where carbon is the first member of a hydrocarbon chain. Thus it is difficult to be certain about the extent of hydrolysis of the methoxy groups and their replacement of hydroxy groups. However the combination of a reduction in the relative intensity of these together with the appearance of the bands characteristic of the hydroxyl groups is clearly the result of a very considerable extent of hydrolysis even if it may not have gone to completion. Generally replicate spectra could be reproduced to within a few wave numbers.

However there appeared to be one significant alteration as the thickness of the film varied which was observed from a number of spectra. The broad band around 3400 cm^{-1} moved to a lower wave number as the thickness decreased. Since this band arises from the hydroxyl groupings this strongly suggests alterations in the hydrogen bonding. These results are summarised in the Table and are illustrated in Figure 2.

This shift of frequency to lower values normally corresponds to a loss of freedom of the hydroxyl group and increasing hydrogen bonding and especially to chelation where the group is most tightly bound.

Thus these results are consistent with and support the earlier suggestions that the film of a silane primer on an aluminium surface is bound to the metal by chemical bonds through hydroxyl groups resulting from hydrolysis of the methoxy groups of the original silane. There is also some evidence of lateral cross-linking of the silane by Si—O—Si bonding. Only when the silane film is just a very few molecules thick is this hydroxyl bonding dominant so that a strong coherent layer is formed.

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