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Reflection-absorption FT-IR studies of the specific interaction of amines and an epoxy adhesive with GPS treated aluminium surfaces

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Abstract

Aluminium surfaces were silanised with γ-glycidoxypropyltrimethoxysilane and the silane films were then further treated with different amines. Investigation before and after treatment, using reflection-absorption FT-IR spectroscopy, strongly indicated that a chemical reaction between the amines and the silane films took place, as observed in the intensity reduction of the epoxy band at 910 cm^{-1}. Increased SiOSi crosslink density was also observed. Treatment with dicyandiamide also showed the appearance of a band which was assigned to the formation of a covalent bond between the curing agent and the epoxy ring of the silane. The results partly explains the improved durability of GPS treated aluminium surfaces after bonding with one-component epoxy adhesives.

Keywords: A. Epoxides; C. Infrared spectra; D. Adhesion by chemical bonding; γ-Glycidoxypropyltrimethoxysilane

1. Introduction

Adhesives have been used for many years in industrial applications, where high durability bonded aluminium structures can be obtained by using adhesives based on, e.g., epoxy resins [1]. Unfortunately, it is necessary to use expensive surface pretreatment processes to obtain the required long-term service life of the bonded joints [2]. Chromium-based processes, such as the chromic-sulphuric acid FPL etch, are extensively used in the aerospace industry. However, hexavalent chromium is reported to be toxic to most living species [3]. Environmental factors together with stricter legislation has therefore led researchers to look for alternative, more environmentally friendly, pretreatment processes.

Organofunctional silanes are widely used as coupling agents to enhance the durability of adhesive joints [4]. The silanes generally have a hydrolysable group (e.g. –OCH$_3$) and an organofunctional group (e.g. an epoxy group) usually selected to be chemically reactive with a given adhesive. After the hydrolysis reaction, the silane can enable the formation of strong Al–O–Si bonds between the hydroxyl groups on the metal surface and the hydrolysed groups of the silane. Hence, a silane coupling agent will perform two functions in order to improve the environmental durability of a bonded joint [5]. Firstly, it will increase the density of strong bonds between the oxide and the adhesive. Secondly, it will improve the hydrolytic stability of the aluminium oxide. Formation of a weak hydrated layer on the aluminium surface is significantly hindered by the formation of a cross-linked multilayer film [2,6,7].

One of the most commonly used silanes is γ-glycidoxypropyltrimethoxysilane (GPS). The treatment of aluminium surfaces with aqueous solutions of GPS before adhesive bonding has been shown to improve bond durability [6–10], and the deposition of GPS and the films formed by GPS on aluminium surfaces have been investigated with a variety of techniques, including FT-IR spectroscopy, X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry [11–22]. Abel et al. [15] used the latter technique to show that the strong Al–O–Si bond is formed between hydrolysed GPS and aluminium surfaces.

Adhesive joints made of aluminium alloy AA6060 and XD4600 epoxy adhesive have in previous work been shown to give improved durability after silanisation with GPS of the substrates to be bonded [23]. The general understanding is that silanisation improves durability

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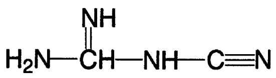
through the formation of strong, covalent bonds between the aluminium surface and the adhesive. By far the most common curing agents used with epoxy-based adhesives are amines [24]. Therefore, in this work GPS films on aluminium surfaces were further treated with different amines and an epoxy adhesive in order to investigate the chemical interactions between the two phases and in order to get a better understanding of the effects amines have on GPS films. Analysis of the GPS films was performed with FT-IR spectroscopy in the reflection mode. Any detected chemical interactions between the amines and the GPS films can possibly, at least partially, explain why silanisation with GPS gives the observed improved durability.

Dicyandiamide (DICY) shown in Fig. 1, is one of the most widely used latent hardeners for epoxy resins, and it is the most common agent for high-temperature curing of one-component adhesive formulations [24,25]. The curing agent will not dissolve in the epoxy resins at low temperatures, and the adhesives are therefore cured at high temperatures where DICY dissolves and reacts chemically with the resins. The curing mechanism of epoxy resins by DICY has been studied in detail by Zahir [25] and Saunders et al. [26]. The chemical interactions between DICY and GPS films are of particular interest. DICY was therefore deposited onto GPS silanised surfaces, and the specimens were heat-treated in order to simulate the curing conditions of a one-component structural epoxy adhesive. One important question mark is whether covalent bonding between DICY and the GPS film, resulting in the formation of strong bonds between the aluminium surface and the adhesive, takes place or not.

2. Experimental

2.1. Materials

The substrate material used in this study was extruded aluminium alloy AA6060-T6, supplied by Hydro Aluminium, Tønder, Denmark. GPS was obtained from Witco Europe SA (Trade Name: Silquest A-187), DICY and dimethylformamide (DMF) from Fluka, ethanolamine from Janssen Chimica, dimethylbenzylamine from Aldrich and the two-component epoxy adhesive Araldite 2020 from Ciba. The curing agent of Araldite 2020 contains isophoronediamine. The one-component structural epoxy adhesive XD4600, was delivered by Dow Automotive, Freienbach, Switzerland. XD4600 contains DICY curing agent.



$H_2N-\overset{\overset{NH}{\|}}{C}H-NH-C\equiv N$

Fig. 1. The chemical structure of DICY.

2.2. Specimen preparation and surface treatment

Aluminium specimens of size $50 \times 25\ mm^2$ were prepared by a successive sequence of abrasion with a ScotchBrite® scouring pad (3M), solvent degreasing with a paper tissue soaked in acetone, and alkaline etching, before further treatment. The etching process was performed in 10 wt% NaOH at 60°C for 50 s. The specimens were then rinsed in 1 wt% HNO_3 at room temperature for 5 min, and in distilled water at room temperature for 10 min. They were then dried at 60°C.

Silanisation was performed in a 1 wt% solution of GPS in distilled water. The pH of the solution was adjusted to 5.0 using acetic acid, and the solution was then continuously stirred for 60 min at ambient temperature, using a magnetic stirrer, for hydrolysis of the silane methoxy groups. The silane was then deposited on the aluminium substrates by immersing them in the solution for 10 min, after which they were dried at 93°C for 60 min. In order to follow the condensation process of the SiOH silanols, one specimen was placed into the FT-IR spectrometer directly after the deposition step. The ambient conditions in the test chamber were 25°C and 35% relative humidity.

GPS silanised aluminium surfaces were treated with different amines or adhesives in order to investigate the chemical interactions of the amines/adhesives with the GPS films. The latent curing agent DICY was deposited onto the GPS silanised specimens by immersing the specimens into a 1 wt% solution in DMF at ambient temperature for a period of 20 min. The specimens were then dried at 40°C for 1 h in order to drive off the solvent, after which the specimens were heat-treated at 180°C for 30 min (typical curing conditions for one-component epoxy adhesives). After they had cooled to room temperature, the specimens were extracted with DMF to remove unreacted DICY from the surface. They were then once again dried at 40°C for 1 h before analysis by FT-IR spectroscopy. XD4600 epoxy adhesive was also deposited onto the GPS silanised specimens from a 1 wt% solution in DMF. However, in order to remove adhesive fillers the solution was filtered with a Millipore Millex-FH filter.

GPS films were also treated with ethanolamine, dimethylbenzylamine and the curing part of Araldite 2020 epoxy adhesive. The ethanolamine treatment was conducted by immersing the specimens into pure ethanolamine at 60°C for 60 min, while treatment with dimethylbenzylamine was performed in a 1% solution in methanol at 60°C for 60 min. Dimethylbenzylamine is a common tertiary amine catalyst used in epoxy adhesive systems. The GPS films were coated with the curing part of Araldite 2020 and heat-treated at 60°C for 3 h (recommended curing cycle for Araldite 2020). The curing part contains isophoronediamine and trimethylhexamethylenediamine. After these different treatments the specimens were extracted with methanol and dried at 40°C for 1 h before analysis by FT-IR spectroscopy. GPS films were also treated with pure DMF and pure methanol, according to the procedures described above, for reference purposes.

A GPS gel was prepared from a 30 wt% solution of GPS at pH 5.0. The hydrolysed solution was dried at 93°C, and the dried gel was ground up, baked into a KBr-pellet and analysed with FT-IR spectroscopy. The dried gel was also reacted with ethanolamine at 60°C.

2.3. *Reflection-absorption infrared spectroscopy*

The treated aluminium specimens were investigated with reflection-absorption infrared (RAIR) spectroscopy. The analysis was performed with a Perkin-Elmer 1725X FT-IR spectrometer where the specimens were mounted on an external reflectance accessory. The spectra was recorded as an average of 100 scans with a resolution 4 cm^{-1} in the range 400–4000 cm^{-1}. However, when following the SiOH condensation process only 10 scans were recorded for each analysis. The angle of the infrared beam to the normal of the specimen surface was 80°. A bare aluminium specimen (not treated with GPS) was used to obtain a background spectrum for the RAIR analysis. Transmission infrared spectra were obtained by deposition of the chemical compound on KBr-pellets.

3. Results

The transmission infrared spectrum of GPS is shown in Fig. 2. Two of the most interesting bands in the spectrum can be identified as $SiOCH_3$ methoxy groups at 822 cm^{-1} and epoxy rings at 910 cm^{-1}. The silane undergoes chemical changes during the hydrolysis and drying processes. During hydrolysis of the silane the $SiOCH_3$ groups will transform into SiOH silanols. These silanols will condense during the drying step, resulting in the formation of a cross-linked SiOSi network. In the dried GPS films (as shown in Fig. 2) the bands in the range 1000–1130 cm^{-1} are mainly attributed to SiOSi vibrations, while the broad band at 3370 cm^{-1} is attributed to SiOH silanols.

The condensation process of the SiOH silanol groups was monitored by placing a silanised specimen in the FT-IR spectrometer directly after the deposition step. As can be seen from Fig. 3, no band was present at 822 cm^{-1}, indicating full hydrolysis of the methoxy groups. Two strong bands could be seen at 919 and 1105 cm^{-1}. These bands are attributed to SiOH and SiOSi groups, respectively. The intensity of the band at 919 cm^{-1} decreased with time, and it was also shifted towards a lower wavenumber, while the intensity of the band at 1105 cm^{-1} increased and was shifted towards a higher wavenumber. The latter indicates a higher density of SiOSi linkages, and thus a higher degree of crosslink density in the film. The condensation process, which started immediately after deposition, was monitored for 4 h, at which time it had declined considerably. However, a post-drying at 93°C for 60 min had a significant effect, resulting in further condensation. After post-drying the two bands were shifted to 910 and 1126 cm^{-1}, and the intensity of the former band was significantly lower than before drying. Similar spectra of GPS films were obtained by drying at 93°C directly after the deposition step (Figs. 4–7). However, the SiOH band at 3370 cm^{-1} was sometimes not detectable, indicating that almost all SiOH groups were consumed during the drying process.

All GPS films that were treated with different amines showed a significant reduction of the band at 910 cm^{-1} compared with the untreated GPS films (Figs. 4–7). Another change that was common for all amine treatments was the shift of the band at 1120 cm^{-1} towards a higher wavenumber. However, treatment with DICY also resulted in one specific change. After

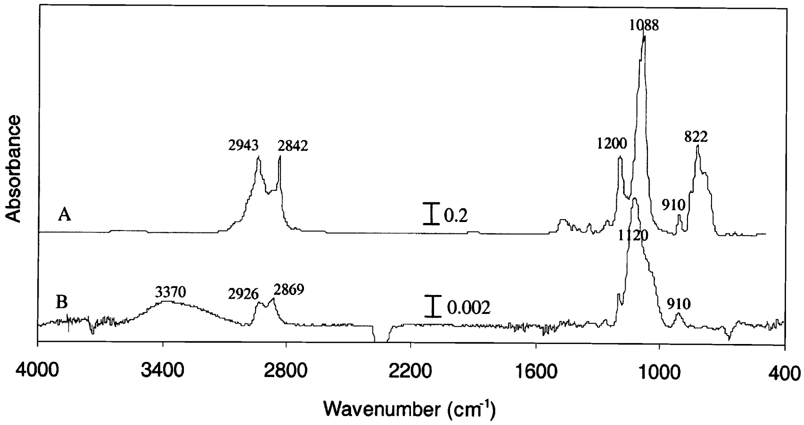


Fig. 2. (A) Transmission infrared spectrum of GPS on KBr-pellet and (B) a typical reflection-absorption infrared spectrum of a dried GPS film on AA6060-T6 aluminium deposited from a 1% solution of GPS in water.

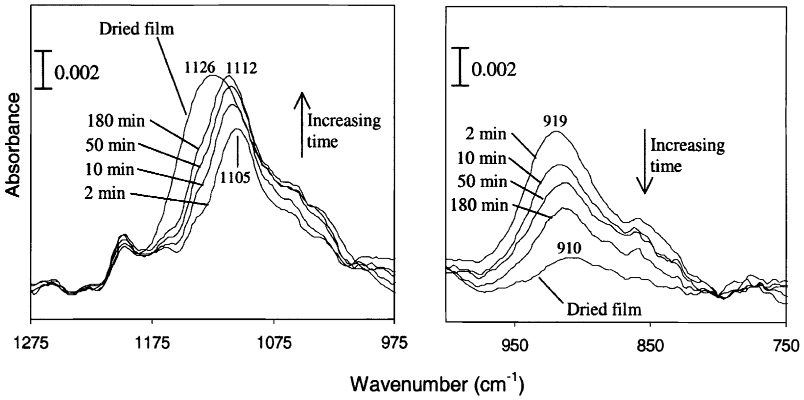


Fig. 3. Reflection-absorption infrared spectra of the condensation process of hydrolysed GPS on AA6060-T6 aluminium deposited from a 1% solution of GPS in water. The ambient conditions were 25°C and 35% relative humidity. The spectra have been shifted vertically for clarity.

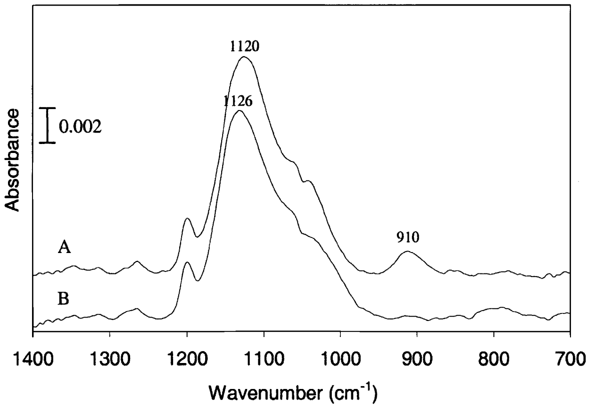


Fig. 4. Reflection-absorption infrared spectra of GPS films on AA6060-T6 aluminium deposited from a 1% solution of GPS in water: (A) untreated and (B) after further treatment with DICY curing agent deposited from a 1% solution in DMF.

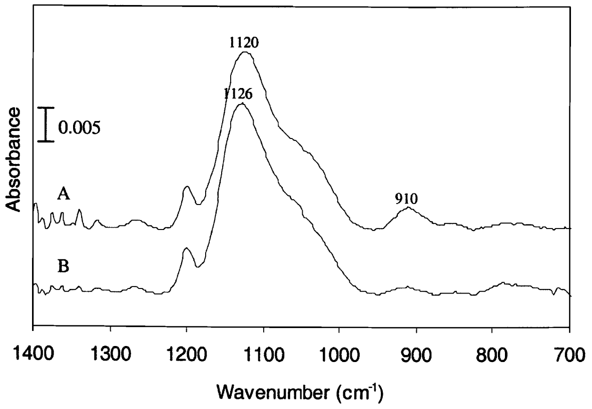


Fig. 5. Reflection-absorption infrared spectra of GPS films on AA6060-T6 aluminium deposited from a 1% solution of GPS in water: (A) untreated and (B) after further treatment with ethanolamine.

treatment, a minor band was observed at 2190 cm^{-1} (Fig. 9). Reference specimens that were treated with pure DMF or pure methanol did not show any significant changes in the RAIR spectra. Hence, neither treatment with solvent nor heat-treatment at 180°C had effect on the structure of the GPS films.

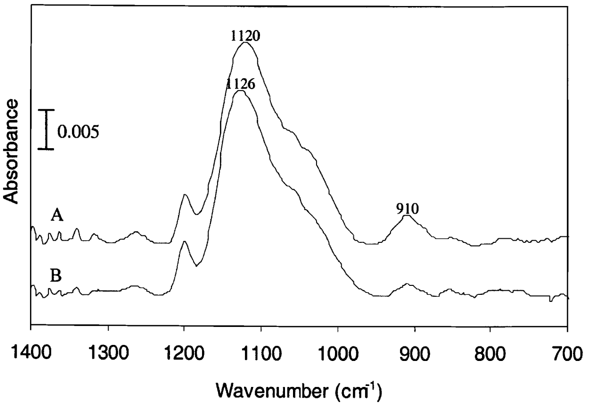


Fig. 6. Reflection-absorption infrared spectra of GPS films on AA6060-T6 aluminium deposited from a 1% solution of GPS in water: (A) untreated and (B) after further treatment with 1% dimethylbenzylamine in methanol.

Fig. 10 shows the transmission infrared spectra of filtered epoxy adhesive before and after curing at 180°C for 30 min. Most of the bands that are indicative of the epoxy resin did not undergo any changes. The intense bands at 1510 and 1608 cm^{-1} are due to the aromatic ring, while the strong bands at 1184 and 1246 cm^{-1} are from ether and substituted aromatic groups, respectively [27]. However, the epoxy band at 914 cm^{-1} totally disappeared, and the emergence of a broad hydroxyl band at 3385 cm^{-1} indicates opening of the epoxy rings. This is consistent with the disappearance of N–H stretching modes around 3350 cm^{-1}, the nitrile ($C\equiv N$) band at 2210 cm^{-1} and the band of the salt form of DICY ($^{-}N=C=N^{+}$) at 2167 cm^{-1} [28]. Hence, the amine curing agent has reacted chemically with the epoxy resin.

A significant reduction in the band at 910 cm^{-1} was also observed after treatment of a GPS surface with filtered epoxy adhesive (Fig. 11). Increased crosslink

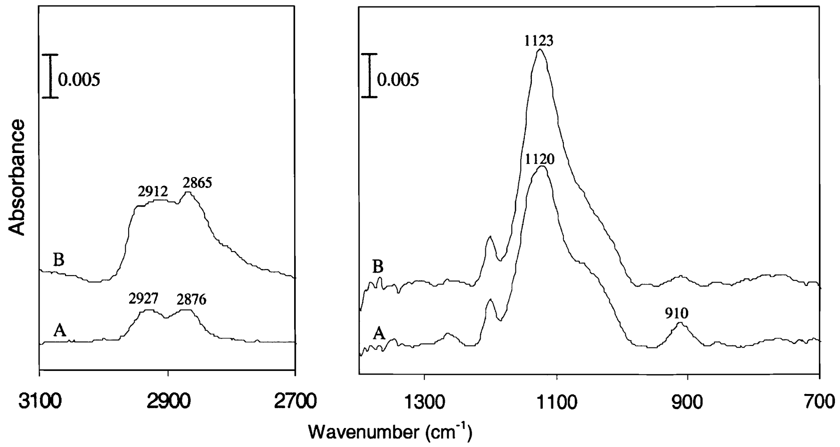


Fig. 7. Reflection-absorption infrared spectra of GPS films on AA6060-T6 aluminium deposited from a 1% solution of GPS in water: (A) untreated and (B) after further treatment with the amine curing agent of Araldite 2020.

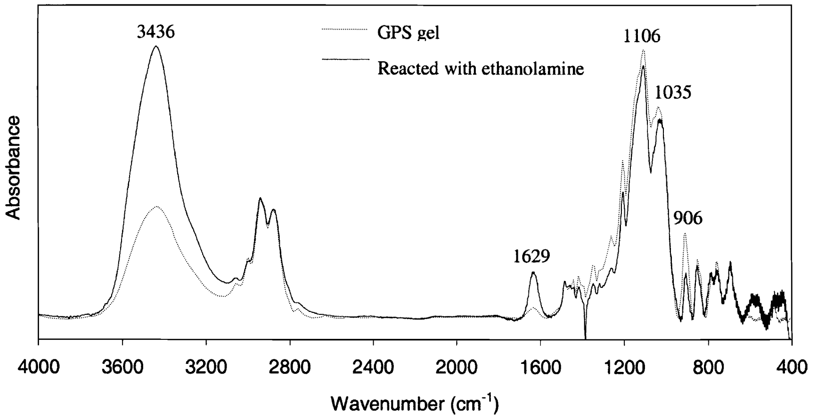


Fig. 8. Transmission FT-IR spectra of GPS gel prepared from a 30% solution in water; before and after reaction with ethanolamine.

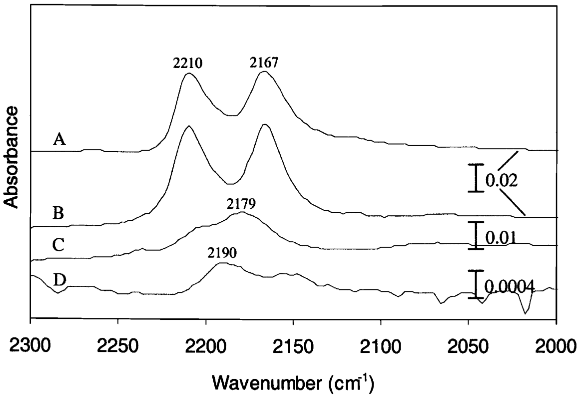
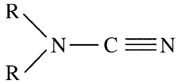


Fig. 9. Infrared spectra in the 2000–2300 cm^{-1} region of: (A) DICY curing agent on AA6060-T6 aluminium; (B) uncured XD4600 epoxy adhesive on KBr-pellet; (C) cured XD4600 epoxy adhesive on KBr-pellet; and (D) DICY treated GPS on AA6060-T6 aluminium.

Table 1
Some of the infrared frequencies discussed in this study

Vibrational assignment	GPS			DICY	Uncured epoxy adhesive
	Bulk	Hydrolysed	Dried film		
$SiOCH_3$	822				
SiOH		919,3370	3370		
SiOSi			1120–1126		
Epoxy ring			910		914
$C\equiv N$				2210	2210
$^{-}N=C=N^{+}$				2167	2167
 $R_2N-C\equiv N$				2190[a]	2179[b]

[a] Present in the spectrum of GPS films after treatment with DICY.
[b] Only present in cured epoxy adhesive.

density was also observed by the shift of the band at 1120 cm^{-1}. The appearance of the two bands indicative of aromatic ether groups at 1510 cm^{-1} and substituted aromatic rings at 1251 cm^{-1} on the treated surface, showed that adhesive was present on the surface after this treatment. The deposited adhesive film was strongly

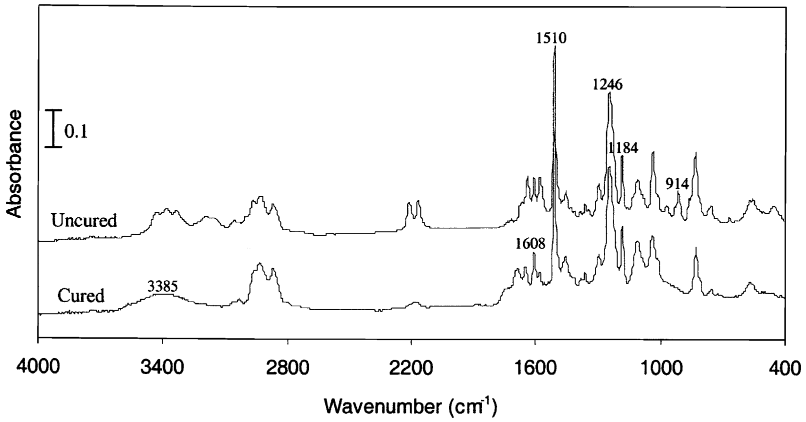


Fig. 10. Transmission infrared spectra of uncured (above) and cured (below) filtered XD4600 epoxy adhesive on KBr-pellets deposited from a 1% solution of XD4600 in DMF.

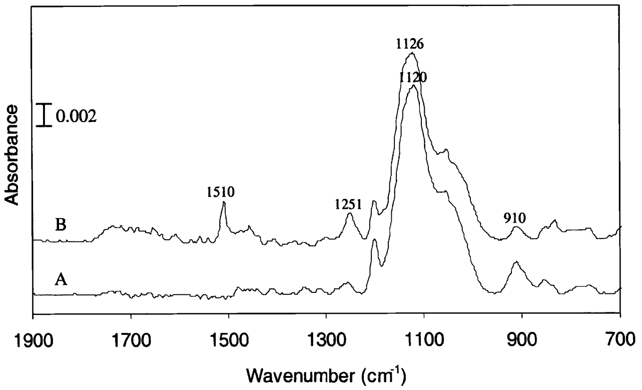


Fig. 11. Reflection-absorption infrared spectra of GPS films on AA6060-T6 aluminium deposited from a 1% solution of GPS in water: (A) untreated and (B) after further treatment with filtered XD4600 epoxy adhesive deposited from a 1% solution in DMF.

bonded to the GPS coated surface, and was not washed away by extraction in DMF.

Some of the infrared frequencies discussed in this study are shown in Table 1.

4. Discussion

Taking into consideration Figs. 2 and 3, both the SiOH group and the epoxy ring have absorbing frequencies in the same region. A major problem with these overlapping absorption bands can be masking of the signal from the epoxy rings, complicating the interpretation of the results. Underhill et al. [14] observed a small peak at 908 cm^{-1}, which was due to the epoxy group in the GPS molecule. This band overlapped with the SiOH peak at 916 cm^{-1}. The presence of two absorbing groups in this region can make it difficult to assign the reduction of a band in this region to the reduction of either SiOH or epoxy groups.

In Fig. 3 the condensation reaction of hydrolysed SiOH groups can be observed. During condensation at room temperature the intensity of the SiOH band at 919 cm^{-1} decreases and is shifted to 914 cm^{-1}. A post-cure at 93°C reduces the intensity further and shifts the band to 910 cm^{-1}. It has been reported that the drying of the GPS film and the condensation of SiOH groups is essentially over within 12 min [11], indicating that the drying process is very rapid at room temperature. This is a much faster drying process than we observed in our study. Fig. 3 shows that the drying process reached a halt after 180 min at an ambient temperature of 23°C and 35% relative humidity. After 240 min no further development was observed. However, the post-drying at 93°C had a significant effect, showing that the drying process was not completed at room temperature.

4.1. Effect of amine treatments

All dried GPS films showed significant changes after amine treatment (Figs. 4–7). It has been proposed that amines can catalyse the condensation reactions of hydrolysed silanes [29]. In this study the treatment of GPS films on aluminium with different amines results in further condensation of the silane film. For all treatments the SiOSi band at 1120 cm^{-1} in the dried films is shifted towards 1126 cm^{-1}, indicating a higher crosslink density. The observed wavenumbers could to some extent vary, but there was always a shift towards higher wavenumbers after the amine treatments. However, although the SiOSi band is shifted, the intensity of this band is only insignificantly altered. One exception was after treatment with the curing part of Araldite 2020 where increased intensity and a shift to 1123 cm^{-1} was observed (Fig. 7). The curing agent contains a band at 1117 cm^{-1}, so this may well be due to the presence of chemically bound curing agent on the surface. Increased intensity of C–H stretching bands in the area 2850–2950 cm^{-1} was also observed.

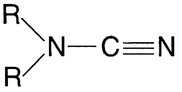
An interesting observation is the intensity reduction of the band at 910 cm^{-1}. Primary amines (e.g. ethanolamine and the curing part of Araldite 2020) are expected to react covalently with epoxy rings, while tertiary amines (e.g. dimethylbenzylamine) are expected to catalyse opening and polymerisation of epoxy rings [30]. Although both the SiOH groups and the epoxy rings have absorbing frequencies in the region around 910 cm^{-1}, here we attribute the observed intensity reduction to the reduction in the number of epoxy rings. We base this assumption on different observations. A shift of the band at 1120 cm^{-1} was observed, but the treatments did not (usually) have any effect on the SiOH band at 3370 cm^{-1}. So it seems that only few SiOH groups were consumed during the amine treatment processes. The main part of the intensity reduction of the band at 910 cm^{-1} must then be due to the consumption of epoxy rings. Thus, there does not seem to be any connection between the intensity reduction of 3370 and 910 cm^{-1} during amine treatments. The intensity reduction was also observed in GPS films where no band at 3370 cm^{-1} was detected, i.e., in films where the condensation process of SiOH groups was almost complete. Still, a band at 910 cm^{-1} was present. Another observation is that during condensation there is a shift of the SiOH band at 919 cm^{-1} towards the band of the epoxy ring at 910 cm^{-1}. This suggests that the band at 910 cm^{-1} in the dried GPS films mainly is the result of absorption from epoxy rings. Also, when a mixture of pure GPS and the curing part of Araldite 2020 was cured at 60°C, the band at 910 cm^{-1} disappeared.

For comparison reasons, also a dried GPS gel was analysed with FT-IR spectroscopy. The spectrum contains a strong O–H stretching band at 3436 cm^{-1} and the epoxy ring/SiOH band at 906 cm^{-1} (Fig. 8). Also, two strong bands appear at 1106 and 1035 cm^{-1}, of which the latter peak is unresolved in the spectra of the GPS films. These bands are attributed to SiOSi vibrations, since longer or more branched siloxane chains result in a broader and more complex SiOSi absorption, with two or more absorbing bands. Some interesting observations were made when reacting the GPS gel with ethanolamine. The intensity of the O–H band at 3436 cm^{-1} was significantly increased, while the intensity of the epoxy/SiOH band at 906 cm^{-1} was significantly decreased (Fig. 8). This shows that a reaction between the epoxy rings and the amine groups in ethanolamine has taken place. The increased intensity of the 3436 cm^{-1} band is due to hydroxyls produced during opening of the epoxy rings and from hydroxyls in the chemically bonded ethanolamine molecules. The remaining part of the 906 cm^{-1} band may be unreacted SiOH groups. These observations support the assumption that the epoxy rings in the GPS films have reacted with amines during the amine treatments. The N–H band at 1629 cm^{-1} also indicates the reaction of the epoxy rings. However, increased crosslink density in the GPS gel was not observed after treatment with ethanolamine.

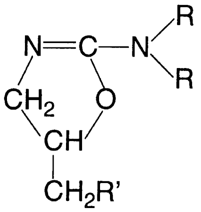
4.2. Treatment with DICY and epoxy adhesive

The reaction between the GPS silanised surface and DICY or an epoxy adhesive can be compared with the reactions taking place during curing of the adhesive. Fig. 10 shows the transmission infrared spectra of filtered epoxy adhesive before and after cure. Most of the bands which are indicative of the epoxy resin do not undergo any changes, i.e. the bands at 1246 and 1510 cm^{-1}. However, the epoxy band at 914 cm^{-1} totally disappears, and the emergence of a broad hydroxyl band at 3385 cm^{-1} indicates opening of the epoxy ring. This is consistent with the disappearance of N–H stretching modes around 3350 cm^{-1}, the nitrile $(\mathrm{C}\equiv\mathrm{N})$ band at 2210 cm^{-1} and the band of the salt form of DICY $(^{-}\mathrm{N}=\mathrm{C}=\mathrm{N}^{+})$ at 2167 cm^{-1} [28]. Thus, the amine curing agent has reacted chemically with the epoxy rings in the resin.

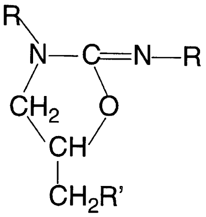
The curing mechanism of epoxy resins by DICY has been studied in detail by Zahir [25] and Saunders et al. [26]. According to Zahir, the reaction of phenyl glycidyl ether with DICY leads mainly to products with two different structural units, namely a dialkyl cyanamide:



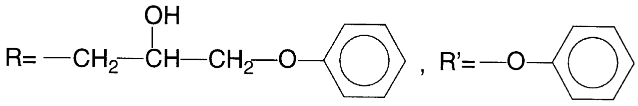
and an organic base, derivatives of 2-amine-2-oxazoline (or its tautomer 2-imino-oxazolidine):



or



where



In addition, urea carbonyl and urethane ester groups may be formed in the resin via the intramolecular and/or intermolecular rearrangement reactions of the above products. We expect that the glycidyl groups of GPS can interact with DICY in the same manner as the glycidyl groups of epoxy resins. Hence, molecular structures as shown above can be expected in a chemical reaction between GPS and DICY.

Fig. 9 depicts the infrared spectra in the 2000–2300 cm^{-1} region of DICY deposited onto aluminium, of uncured and cured epoxy adhesive, and of a GPS surface treated with DICY. The DICY treated GPS surface was extracted with DMF solvent after heat-treatment at 180°C in order to remove loosely adsorbed DICY before analysis with FT-IR. Both the $C\equiv N$ band at 2210 cm^{-1} and the $^{-}N=C=N^{+}$ band at 2167 cm^{-1} are present in the spectra of DICY and epoxy adhesive. After curing of the adhesive, a new band is formed in the region between the two original bands, namely at 2179 cm^{-1}. A band in the same region also appears on the GPS surface after treatment with DICY. This band at 2190 cm^{-1} is not present on the surface before treatment with DICY or the GPS surface that was treated only with DMF. The band is weak, but it is not present in the spectra of other amine treatments. Other authors have attributed bands in this area to the nitrile group in DICY [25,28,31]. Taking into consideration the work of Zahir [25], here we tentatively assign the band at 2190 cm^{-1} to be the dialkyl cyanamide structure shown above, or possibly an alkyl cyanamide structure, $R\text{-}NH\text{–}C\equiv N$. The shift from 2179 to 2190 cm^{-1} can be explained by the different substituents of the cyanamide in the reaction with either epoxy adhesive or GPS, resulting in altered vibration frequency.

Deposition and curing of an epoxy adhesive film on a GPS coated aluminium surface has the same effect as deposition of DICY followed by heat-treatment at 180°C (Fig. 11). Both an intensity reduction of the epoxy band at 910 cm^{-1}, as well as increased crosslink density was observed. This shows that the curing agent of the epoxy adhesive is responsible for the changes occurring. The presence of an adhesive film on the surface is shown by the ether band at 1251 cm^{-1} and the strong aromatic band at 1510 cm^{-1}. However, the bands at 2179 or 2190 cm^{-1} could not be observed on the surface. The adhesive film is very thin in order to enhance the interface reactions and the signal is possibly too weak for detection of these bands.

As discussed above, treatment with DICY suggested that a covalent bond was formed between DICY and the GPS film. The curing agent will also react chemically with the epoxy resin in the formation of a polymer network, and the presence of a covalent bridge between the aluminium surface and the adhesive can therefore be expected. The existence of a covalent bond between a GPS film on aluminium and an epoxy adhesive has been shown by Rattana et al. [32], using ToF-SIMS. They showed that the amine curing agent interacted covalently with the epoxy ring of the GPS molecule and the DGEBA resin, forming a network of covalent bonds from the aluminium surface through to the bulk of the adhesive. Thus, it is possible for an amine-cured epoxy adhesive system to interact covalently with a GPS film on aluminium. These covalent bonds are of importance with respect to the durability of an adhesively bonded joint, as they introduce stronger bonds between the adhesive and the surface. Degradation of the bonded joint due to the effects of humid environment will then be delayed, resulting in improved durability. This was shown in a previous publication where AA6060-T6 surfaces silanised with GPS was shown to improve durability after bonding with epoxy adhesive [23].

The band at 910 cm^{-1} did not totally disappear during treatment with amines or epoxy adhesive. The silane film exists in the form of a crosslinked siloxane network on the surface, as illustrated by Bell et al. [33], and it is possible that only the epoxy rings in the outer surface layer of the GPS films are accessible for reaction with the curing agent. The thickness of the siloxane network acts as a barrier that prevents diffusion of curing agent towards the surface. Hence, after treatment of the GPS films with amines or adhesive, only the epoxy rings in the outer siloxane layer will react. The epoxy rings closer to the surface are not accessible for chemical reaction. Thus, they will not react and can still be detected after treatment.

5. Conclusion

Alkaline etched surfaces of aluminium alloy AA6060-T6 were coated with GPS and then further treated with different amines. Investigation of the GPS films before and after treatment using RAIR showed that significant changes occurred during the treatments. All amine treatments strongly indicated that a chemical reaction between the amines and the GPS films took place, as observed in the intensity reduction of the epoxy band at 910 cm^{-1}. The amines also catalysed the condensation of SiOH groups, and a higher degree of SiOSi crosslink density was observed in the films.

Treatment with DICY, a common curing agent used in one-component epoxy adhesives, also showed the appearance of a band at 2190 cm^{-1} in addition to increased crosslink density and an intensity reduction at 910 cm^{-1}. The band at 2190 cm^{-1} is indicative of the nitrile $C\equiv N$ group in DICY and is assigned to the formation of a covalent bond between the curing agent and the epoxy ring of the GPS molecule.

Treatment of the GPS films with epoxy adhesive resulted in the same changes as treatment with amines.

The existence of covalent bonds between a GPS film on aluminium and an epoxy adhesive is of importance with respect to the durability of a bonded joint. Stronger bonds are introduced, resulting in improved durability in humid environment. The results from this study explains the improved performance of GPS treated aluminium surfaces reported earlier [23].

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References

[1] Brémont M, Brockmann W. J Adhes 1996;58:69–99.
[2] Kinloch AJ. Proc Inst Mech Eng 1997;211:307–35.
[3] Rogers NL. In: Thrall EW, Shannon RW, editors. Adhesive bonding of aluminium alloys. New York, Basel: Marcel Dekker, 1985.
[4] Horner MR, Boerio FJ, Clearfield HM. In: Mittal KL, editor. Silanes and other coupling agents. Utrecht: VSP, 1992.
[5] Rider AN, Arnott DR, Wilson AR, Vargas O. Mater Sci Forum 1995;189/190:235–40.
[6] Rider AN, Arnott DR. Surf Interface Anal 1995;24:583–90.
[7] Arnott DR, Wilson AR, Rider AN, Lambriandis LT, Farr NG. Appl Surf Sci 1993;70/71:109–13.
[8] Digby RP, Shaw SJ. Int J Adhes Adhes 1998;18:261–4.
[9] Thiedman W, Tolan FC, Pearce PJ, Morris CEM. J Adhes 1987;22:197–210.
[10] Rider AN, Arnott DR. Int J Adhes Adhes 2000;20:209–20.
[11] Underhill PR, Goring G, DuQuesnay DL. Appl Surf Sci 1998;134:247–53.
[12] Underhill PR, Goring G, DuQuesnay DL. Int J Adhes Adhes 1998;18:307–11.
[13] Underhill PR, Goring G, DuQuesnay DL. Int J Adhes Adhes 1998;18:313–7.
[14] Underhill PR, Goring G, DuQuesnay DL. Int J Adhes Adhes 2000;20:195–9.
[15] Abel M-L, Watts JF, Digby RP. Int J Adhes Adhes 1998;18: 179–92.
[16] Abel M-L, Digby RP, Fletcher IW, Watts JF. Surf Interface Anal 2000;29:115–25.
[17] Abel M-L, Rattana A, Watts JF. J Adhes 2000;73:313–40.
[18] Rattana A, Abel M-L, Watts JF. In: Proceedings of the 24th Annual Meeting of the Adhesion Society, Williamsburg, 2001. p. 202.
[19] Leung YL, Zhou MY, Wong PC, Mitchell KAR. Appl Surf Sci 1992;59:23–9.
[20] Woods GA, Haq S, Richardson NV, Shaw S, Digby R, Raval R. Surf Sci 1999;433–5:199–204.
[21] Bertelsen CM, Boerio FJ. Prog Org Coat 2001;41:239–46.
[22] Kono M, Sun X, Li R, Wong KC, Mitchell KAR, Foster T. Surf Rev Lett 2001;8:43–50.
[23] Johnsen BB, Olafsen K, Stori A, Vinje K. J Adhes Sci Technol 2002;16:1931–48.
[24] Pocius AV. Adhesion and adhesives technology. Munich: Carl Hanser, 1997.
[25] Zahir SA. Adv Org Coat Sci Technol 1982;4:83–102.
[26] Saunders TF, Levy MF, Serino JF. J Polym Sci 1967;5:1609–17.
[27] Hong S-H, Tsai J-S. Macromol Mater Eng 2000;276/277:59–65.
[28] Fondeur F, Koenig JL. Appl Spectrosc 1993;47:1–6.
[29] Osterholtz FD, Pohl ER. J Adhes Sci Technol 1992;6:127–49.
[30] Brydson JA. Plastics materials. London: Butterworth & Co Ltd., 1975.
[31] Carter RO, Dickie RA, Holubka JW, Lindsay NE. Ind Eng Chem Res 1989;28:48–51.
[32] Rattana A, Hermes JD, Abel M-L, Watts JF. Int J Adhes Adhes 2002;22:205–18.
[33] Bell JP, Schmidt RG, Malofsky A, Mancini D. In: Mittal KL, editor. Silanes and other coupling agents. Utrecht: VSP, 1992. p. 241.